

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

In re application of:
James M. Tour, *et al.*

Serial No. 10/561,253

Filed: December 19, 2005

Title: POLYMERIZATION INITIATED AT
SIDEWALLS OF CARBON NANOTUBES

§ Before the Examiner:
§ William K. Cheung
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§ Group Art Unit: 1796
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§ Conf. No.: 6532
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APPEAL BRIEF

MAIL STOP: Appeal Brief-Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Appellants file the following Appeal Brief and respectfully request that the Board overturn the Examiner's thirty claim rejections under 35 U.S.C. § 103(a), allowing all pending claims to issue.

Appellants submit the small entity fee of \$270 for the filing of this Appeal Brief, as set forth in 37 CFR 41.20(b)(2). If any other fees are due and are not included, the Director is authorized to charge any fees or credit any overpayment to Deposit Account No. 23-2426 of Winstead PC (referencing matter number 11321-P068WOUS).

I. REAL PARTY IN INTEREST

The real parties in interest are William Marsh Rice University, a university having an address of 6100 Main St., Houston, TX 77005 and the University of Houston, a university having an address of 4800 Calhoun Rd., Houston, TX 77004. Said Universities are the joint assignees of the invention.

II. RELATED APPEALS AND INTERFERENCES

The Appellants, the Appellants' legal representatives and the assignees are presently unaware of any related appeals or interferences which will directly affect, be directly affected by, or have a bearing on the Board's decision in the pending appeal. The Board will be notified by at least one of the aforementioned parties should this situation change.

III. STATUS OF CLAIMS

Claims 2 – 6, 8 – 28 and 31 – 34 are pending. Claims 1, 7, 29 and 30 are cancelled.

Claims 2 – 6, 8 – 28 and 31 – 34 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over International Patent Application Publication WO 02/060812 (hereinafter, *Tour*) and United States Patent 3,554,992 (hereinafter, *Lamb*).

Claims 2 – 6, 8 – 28 and 31 – 34 remain under consideration in the Application. Claims 2 – 6, 8 – 28 and 31 – 34 are appealed and are presented in the attached CLAIMS APPENDIX.

IV. STATUS OF AMENDMENTS

The claims presented herein are those existing at the time of the Final Office Action mailed April 6, 2010. All requested claim amendments have been entered and no further amendments are required.

V. SUMMARY OF CLAIMED SUBJECT MATTER

V.1 Independent Claim 2

Independent claim 2 recites a method comprising:

- a) providing aryl halide functionalized carbon nanotubes, where the halide is selected from chlorine, bromine, iodine, and combinations thereof;
- b) dispersing the aryl halide functionalized carbon nanotubes in a solvent;
- c) adding an alkyllithium species to the solvent that reacts with the aryl halide functionalized carbon nanotubes, thereby forming an aryl-lithium species comprising a polymerizable species on the carbon nanotubes that has aryl-lithium covalent bonds;
- d) adding a monomer to the solvent; and
- e) initiating a polymerization reaction between the monomer and the polymerizable species to form a polymer-carbon nanotube material, where the polymer is covalently bound to the carbon nanotubes and the polymerization reaction is selected from anionic polymerization and ring opening polymerization.

Support for the aryl halide functionalized carbon nanotubes of a) may be found in at least paragraphs [0012], [0021] and [0032], as well as original claim 7. Support for dispersion in a solvent, as recited in b), may be found in at least paragraph [0022]. Support for addition of the alkyllithium species of c) to form an aryl-lithium species on the carbon nanotubes may be found in at least paragraphs [0012] and [0022] and Figure 1. Support for addition of a monomer, as recited in d), may be found in at least paragraph [0023] and Figure 1. Support for initiating an anionic or ring opening polymerization reaction between the monomer and the polymerizable species, as recited in e), to form a polymer-carbon nanotube material having the polymer covalently bound to the carbon nanotubes may be found in at least paragraphs [0012], [0024], [0030], [0034] and [0037] and Figure 1.

V.2 Independent Claim 3

Independent claim 3 recites a method comprising:

- a) providing aryl halide functionalized carbon nanotubes, where the halide is selected from chlorine, bromine, iodine, and combinations thereof;
- b) dispersing the aryl halide functionalized carbon nanotubes in a solvent;
- c) adding a metal to the solvent that reacts with the aryl halide functionalized carbon nanotubes, thereby forming an aryl-metal species comprising a polymerizable species on the carbon nanotubes that has aryl-metal covalent bonds;
- d) adding a monomer to the solvent; and
- e) initiating a polymerization reaction between the monomer and the polymerizable species to form a polymer-carbon nanotube material, where the polymer is covalently bound to the carbon nanotubes and the polymerization reaction is selected from anionic polymerization and ring opening polymerization.

Support for the aryl halide functionalized carbon nanotubes of a) may be found in at least paragraphs [0012], [0021] and [0032], as well as original claim 7. Support for dispersion in a solvent, as recited in b), may be found in at least paragraph [0022]. Support for adding a metal to the solvent, as recited in c), may be found in at least paragraphs [0012] and [0026] and Figure 2. Support for addition of a monomer, as recited in d), may be found in at least paragraph [0023] and Figure 2. Support for initiating an anionic or ring opening polymerization reaction to form a polymer-carbon nanotube material having the polymer covalently bound to the carbon nanotubes may be found in at least paragraphs [0012], [0024], [0030], [0034] and [0037] and Figure 2.

V.3 Independent Claim 10

Independent claim 10 recites a method comprising:

- a) providing functionalized carbon nanotubes comprising nucleation sites operable for initiating a polymerization reaction after deprotonation to form initiator

groups, where the polymerization reaction is an anionic polymerization or a ring opening polymerization;

- b) dispersing the functionalized carbon nanotubes in a solvent;
- c) adding a deprotonating agent to the solvent that deprotonates the nucleation sites to form initiator groups operable for initiating the polymerization reaction;
- d) adding a monomer to the solvent; and
- e) initiating a polymerization reaction between the monomer and the initiator groups to form a polymer-carbon nanotube material, where the polymer is covalently bound to the carbon nanotubes and the polymerization reaction is an anionic polymerization or ring opening polymerization.

Support for the functionalized carbon nanotubes of a) having nucleation sites operable for forming initiator groups after deprotonation may be found in at least paragraphs [0012], [0027], [0028], [0032] and [0038] and Figure 3. Support for dispersion in a solvent, as recited in b), may be found in at least paragraph [0022]. Support for adding a deprotonating agent to the solvent, as recited in c), to deprotonate the nucleation sites and form initiator groups may be found in at least paragraphs [0012], [0028] and [0038] and Figure 3. Support for addition of a monomer, as recited in d), may be found in at least paragraph [0023] and Figure 3. Support for initiating an anionic or ring opening polymerization reaction between the monomer and the initiator groups to form a polymer-carbon nanotube material having the polymer covalently bound to the carbon nanotubes may be found in at least paragraphs [0012], [0028], [0038] and Figure 3.

V.2 Dependent Claims 4 – 6, 8, 9, 11 – 28 and 31 – 34

Claims 4 – 6, 8, 9, 11 – 28 and 31 – 34 depend either directly or indirectly from at least one of independent claims 2, 3 and 10 and are directed to various embodiments further defining the claimed methods.

V.2.1 Claim 4

Claim 4 depends from claim 3 and recites that the metal is selected from zinc, nickel,

potassium, sodium, lithium, magnesium, cesium, palladium and combinations thereof. Support for the claimed metals may be found in at least paragraph [0026] and Figure 2.

V.2.2 Claim 5

Claim 5 depends from claim 3 and recites that the metal is Mg, where the aryl-metal bonds are aryl-Mg bonds comprising a Grignard species. Support for aryl-Mg bonds comprising a Grignard species may be found in at least paragraph [0026] and Figure 2.

V.2.3 Claim 6

Claim 6 depends from any one of claims 2 – 5 and recites that the aryl halides are bonded to a sidewall of the aryl halide functionalized carbon nanotubes. Support for sidewall aryl halides may be found in at least paragraphs [0003], [0020], [0021], [0032] and [0034] and Figures 1 and 2.

V.2.4 Claim 8

Claim 8 depends from any one of claims 2 – 5 and recites that the aryl halide is an aryl bromide. Support for an aryl bromide may be found in at least paragraphs [0012] and [0021] and Figures 1 and 2.

V.2.5 Claim 9

Claim 9 depends from claim 2 and recites that the alkyllithium species is n-butyllithium. Support for n-butyllithium may be found in at least paragraph [0022].

V.2.6 Claim 11

Claim 11 depends from claim 10 and recites that the nucleation sites comprise at least one element selected from carbon, sulfur, oxygen and nitrogen. Support for the claimed elements comprising a nucleation site may be found in at least paragraph [0027].

V.2.7 Claim 12

Claim 12 depends from claim 10 and recites that the functionalized carbon nanotubes are

selected from phenol functionalized carbon nanotubes, thiophenol functionalized carbon nanotubes, phenethyl alcohol functionalized carbon nanotubes (CNT-C₆H₄-CH₂CH₂OH), CNT-C₆H₄-NHBoc, and combinations thereof. Support for the claimed functionalized carbon nanotubes may be found in at least paragraph [0027].

V.2.8 Claim 13

Claim 13 depends from any one of claims 10 – 12 and recites that the nucleation sites are on the sidewall of the functionalized carbon nanotubes. Support for sidewalls may be found in at least paragraphs [0020], [0021], [0032] and [0034] and Figure 3.

V.2.9 Claim 14

Claim 14 depends from any one of claims 10 – 12 and recites that the deprotonating agent comprises a base. Support for a basic deprotonating agent may be found in at least paragraph [0028].

V.2.10 Claim 15

Claim 15 depends from claim 14 and recites that the base is selected from KOH, KH, NaOH, NaH and potassium hexamethyldisilazide. Support for the claimed bases may be found in at least paragraph [0028].

V.2.11 Claim 16

Claim 16 depends from any one of claims 10 – 12 and recites that the deprotonating agent comprises a metal operable for deprotonating the nucleation sites. Support for a metallic deprotonating agent may be found in at least paragraph [0028].

V.2.12 Claim 17

Claim 17 depends from claim 16 and recites that the metal is selected from zinc, nickel, potassium, sodium, lithium, magnesium, cesium, palladium and combinations thereof. Support for the claimed metals may be found in at least paragraph [0028].

V.2.13 Claim 18

Claim 18 depends from any one of claims 2 – 5 or 10 – 12 and recites that the initiating step comprises initiating anionic polymerization. Support for anionic polymerization may be found in at least paragraphs [0003], [0012], [0024], [0025], [0028] and [0032].

V.2.14 Claim 19

Claim 19 depends from any one of claims 2 – 5 or 10 – 12 and recites that the initiating step comprises ring opening polymerization. Support for ring opening polymerization may be found in at least paragraphs [0003], [0012] and [0030].

V.2.15 Claim 20

Claim 20 depends from any one of claims 2 – 5 or 10 – 12 and recites that the functionalized carbon nanotubes are single-wall carbon nanotubes. Support for single-wall carbon nanotubes may be found in at least paragraphs [0021] (the HiPco process produces single-wall carbon nanotubes), [0030], [0034] and [0037].

V.2.16 Claim 21

Claim 21 depends from any one of claims 2 – 5 or 10 – 12 and recites that the solvent is tetrahydrofuran. Support for a tetrahydrofuran solvent may be found in at least paragraph [0022] and Figures 1 – 3.

V.2.17 Claim 22

Claim 22 depends from any one of claims 2 – 5 or 10 – 12 and recites that the monomer is selected from styrene, acrylates, methyl acrylates, vinyl acetate, vinyl pyridines, isoprene, butadiene, chloroprene, acrylonitrile, maleic anhydride and combinations thereof. Support for the claimed monomers may be found in at least paragraph [0023].

V.2.18 Claim 23

Claim 23 depends from any one of claims 2 – 5 or 10 – 12 and recites that the monomer comprises styrene. Support for styrene monomer may be found in at least paragraphs [0023] and [0036].

V.2.19 Claim 24

Claim 24 depends from any one of claims 2 – 5 or 10 – 12 and recites that the methods further comprise adding a terminating agent suitable for terminating the polymerization reaction. Support for adding a terminating reagent may be found in at least paragraph [0025].

V.2.20 Claim 25

Claim 25 depends from claim 24 and recites that the terminating agent is selected from ethanol, acetaldehyde, trimethylsilyl chloride, and combinations thereof. Support for the claimed terminating agents may be found in at least paragraph [0025].

V.2.21 Claim 26

Claim 26 depends from claim 24 and recites that the terminating agent is ethanol. Support for ethanol as a terminating agent may be found in at least paragraph [0025].

V.2.22 Claim 27

Claim 27 depends from any one of claims 2 – 5 or 10 – 12 and recites that a concentration of the monomer is between about 0.03 and about 0.16 g/mL. Support for the claimed range may be found in at least paragraph [0023].

V.2.23 Claim 28

Claim 28 depends from any one of claims 2 – 5 or 10 – 12 and recites that the initiating step occurs at a temperature between about 0°C and about 50°C. Support for the claimed range may be found in at least paragraph [0023].

V.2.24 Claim 31

Claim 31 depends from any one of claims 2 – 5 or 10 – 12 and recites that the methods further comprise adding a polymerization catalyst to the solvent. Support for adding a polymerization catalyst may be found in at least paragraphs [0026] and [0030].

V.2.25 Claim 32

Claim 32 depends from claim 31 and recites that the polymerization catalyst comprises TiCl_4 . Support for TiCl_4 as a polymerization catalyst may be found in at least paragraph [0026].

V.2.26 Claim 33

Claim 33 depends from any one of claims 2 – 5 or 10 – 12 and recites that the methods further comprise utilizing the polymer-carbon nanotube material in a drug delivery process. Support for use in a drug delivery process may be found in at least paragraph [0012].

V.2.27 Claim 34

Claim 34 depends from any one of claims 2 – 5 or 10 – 12 and recites that the methods further comprise utilizing the polymer-carbon nanotube material for scaffolding to promote cellular growth. Support for use as scaffolding to promote cellular growth may be found in at least paragraph [0012].

All claims will be argued in this appeal.

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

Appellants respectfully request that the Board review the following grounds of rejection:

Whether claims 2 – 6, 8 – 28 and 31 – 34 are unpatentable under 35 U.S.C. § 103(a) over *Tour* and *Lamb*.

VII. ARGUMENT

Rejection of Claims 2 – 6, 8 – 28 and 31 – 34 Under 35 U.S.C. § 103(a) over *Tour* and *Lamb*

VII.1 Standard of Review

The standard of review for establishing obviousness is set forth as follows: "To establish *prima facie* obviousness of a claimed invention, all features must be taught or suggested by the prior art." *In re Royka*, 490 F.2d 981, 180 U.S.P.Q. 580 (C.C.P.A. 1974). Furthermore, "[r]ejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness". *KSR Int'l Co. v. Teleflex Inc.*, 127 S.Ct. 1727, 1741 (2007) citing with approval *In re Kahn*, 441 F.3d 977, 988 (Fed. Cir. 2006). In addition, in issuing rejections under 35 U.S.C. § 103(a), the Examiner must consider an invention and the prior art as a whole in accordance with the requisite *Graham* factual inquiries. MPEP § 2141; *Ruiz v. A.B. Chance Co.* 69 USPQ2d 1686, 1690 (Fed. Cir. 2004). Obviousness cannot be proven merely by showing that the elements of a claimed device were known in the prior art; it must be shown that those of ordinary skill in the art would have had some apparent reason to combine the known elements in the fashion claimed. *Ex parte Whalen*, 89 USPQ2d at 1084 citing *KSR Int'l Co. v. Teleflex Inc.*, 127 S.Ct. at 1741.

"All words in a claim must be considered in judging the patentability of that claim against the prior art." *In re Wilson*, 424 F.2d 1382, 1385, 165 USPQ 494, 496 (CCPA 1970). "If an independent claim is nonobvious under 35 U.S.C. 103, then any claim depending therefrom is nonobvious." *In re Fine*, 837 F.2d 1071, 5 USPQ2d 1596 (Fed. Cir. 1988).

VII.2 Overview of the Rejections

In the final Office Action mailed April 6, 2010 the Examiner rejected claims 2 – 6, 8 – 28 and 31 – 34 under 35 U.S.C. § 103(a) as being unpatentable over *Tour* and *Lamb*. In particular, the Examiner made the following allegations regarding the independent claims:

1) Regarding independent claims 2 and 3, the Examiner alleged that *Tour* teaches single-wall carbon nanotubes functionalized with aryl chlorine [sic] functionalities. April 6, 2010

Office Action at page 4. In addition, the Examiner alleged that *Tour* teaches that halogenated (fluorinated) carbon nanotubes can participate in reactions with an alkyllithium reagent via a Grignard reaction mechanism. *Ibid.* Further, the Examiner alleged that *Tour* teaches that single-wall carbon nanotubes can undergo various polymerization mechanisms that include anionic polymerization. April 6, 2010 Office Action at pages 4 – 5.

2) Regarding independent claim 10, the Examiner alleged that the feature ‘operable for anionic or ring opening polymerization’ (regarding nucleation sites after deprotonation to form initiator groups) is inherently possessed by *Tour*.

3) The Examiner acknowledged that *Tour* “does not teach the specific mechanism for preparing a polymer.” However, the Examiner alleged that *Lamb* teaches the specifics of using a Grignard reaction for initiating a polymerization process. April 6, 2010 Office Action at page 5. Therefore, the Examiner alleged that one of ordinary skill in the art would have been motivated to incorporate all of the reaction related specifics of *Lamb* into *Tour* to obtain the claimed invention.

In response to Appellants’ prior arguments, the Examiner alleged that the mechanistic features of Figures 1 and 2 from Appellants’ prior response (see April 6, 2010 Office Action at page 8 for Appellants’ Figures 1 and 2, which are also reproduced below and discussed herein) were not reflected in or relevant to the claims. April 6, 2010 Office Action at page 7. In addition, the Examiner failed to understand the significance of Appellants’ Figure 1, which reproduces a portion of the teachings of United States Patent 6,827,918 (hereinafter, *Margrave*) that is referenced by *Tour* and cited by the Examiner. The Examiner acknowledged that a different reaction than that allegedly taught in *Tour* is shown in Figure 1. April 6, 2010 Office Action at page 8. Therefore, the Examiner discounted the significance of Figure 1 toward Appellants’ prior arguments. April 6, 2010 Office Action at page 9.

VII.3 Appellants’ Comments Regarding the Examiner’s Mischaracterization of Tour and Lamb in the April 6, 2010 Office Action

Hereinafter, Appellants will demonstrate for the Board that the Examiner has significantly mischaracterized the teachings of both *Tour* (including teachings of *Margrave*

referenced therein) and *Lamb*. Appellants will particularly demonstrate for the Board that Appellants' Figures 1 and 2 are highly relevant for illustrating the differences between the teachings of *Tour/Margrave* and the claimed invention and that a mechanistic showing is important for understanding the differences therebetween. In addition, Appellants will demonstrate for the Board that *Lamb* teaches a significantly different polymerization process that would not lead to the claimed invention when combined with *Tour*. In providing this showing for the Board, Appellants will first generally demonstrate how the Examiner has mischaracterized the teachings of *Tour/Margrave* and *Lamb* and thereafter apply those remarks to each of the instantly rejected independent claims.

VII.3.1 Appellants' Comments on the Reaction Mechanism and the Teachings of Margrave as Referenced by Tour

Reproduced hereinbelow are Figures 1 and 2 previously presented by Appellants. Appellants' Figure 1 shows a reaction of sidewall fluorinated carbon nanotubes with an alkyl lithium species, which is the reaction of *Margrave* that is referenced by *Tour*. The reaction of sidewall fluorinated carbon nanotubes with an alkyl lithium species depicted in Appellants' Figure 1 is expressly taught by *Margrave* to be a **nucleophilic substitution reaction** (see *Margrave*; Abstract; Column 4, lines 1 – 18; Column 14, lines 51 – 66, and Column 17, line 58 through Column 19, line 6). The **nucleophilic substitution reaction** of *Margrave* is referenced by *Tour* on page 2, lines 13 – 18. This reference from *Tour* was cited by the Examiner to allegedly demonstrate that halogenated carbon nanotubes can participate in reactions with an alkyl lithium reagent via a Grignard reaction mechanism. April 6, 2010 Office Action at page 4. Appellants' Figure 2 illustrates certain details of Appellants' claims 2 and 3, which do **not** involve a nucleophilic substitution process, as discussed hereinafter. The carbon nanotube portions of the aryl halide functionalized carbon nanotubes in Figure 2 have not been shown for purposes of clarity, since the salient chemical transformations take place at the halide group away from the carbon nanotube backbone.

Figure 1

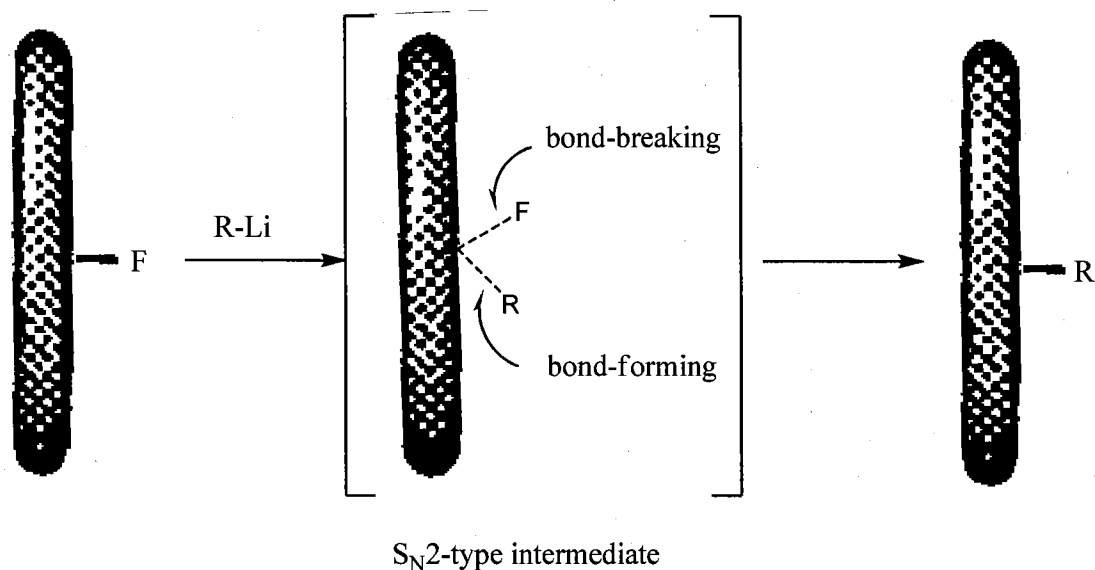
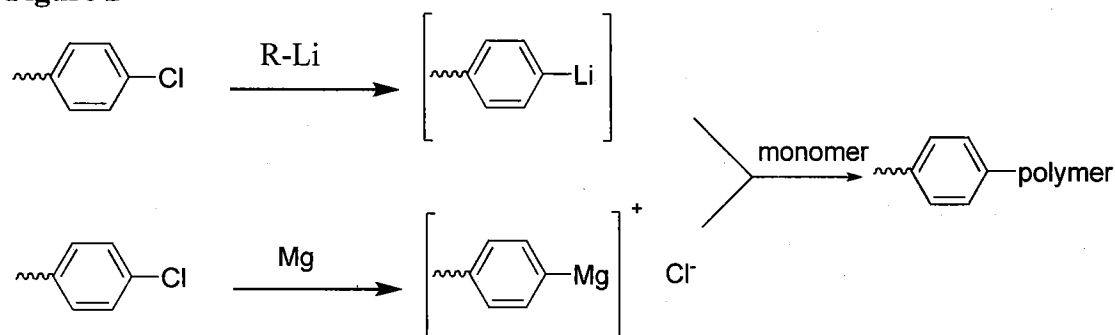


Figure 2



Appellants do not disagree with the Examiner that the claims, as written, do not exclude or require any specific reaction mechanism. Appellants' Figure 2 merely illustrates starting materials (aryl halide functionalized carbon nanotubes), reactive intermediates [an aryl-lithium species for claim 2 and aryl-magnesium (aryl-metal) species for claim 3], and a polymer-carbon nanotube material product that **are** all **claimed** features of claims 2 and 3. In fact, other than showing the **claimed** features of claims 2 and 3, Appellants' Figure 2 in no way shows a

purported mechanism by which the reactions occur. Appellants' Figure 2 was presented by Appellants to distinguish the **claimed** features over the teachings of *Tour* and *Margrave* shown in Appellants' Figure 1. As demonstrated hereinafter, the reaction of *Margrave* that is referenced by *Tour* fails to teach or suggest any of the claimed structural elements.

The Examiner has failed to appreciate or understand why Appellants' Figure 1 was presented and has discounted all of Appellants' arguments referencing the teachings of this Figure as a result. April 6, 2010 Office Action at page 9. As discussed hereinabove, the teachings of *Margrave* as referenced by *Tour* that are shown in Appellants' Figure 1 were cited by the Examiner to establish that halogenated carbon nanotubes "can participate [sic] reactions with an alkyl-lithium reagent (via Grignard reaction mechanism)." In response, Appellants contend that Appellants' Figure 1 is highly relevant to Appellants' argument and clearly demonstrates that key elements of the instantly claimed invention are not taught or suggested by *Tour/Margrave*. In fact, in response to Appellants' prior arguments, the Examiner even acknowledges that "***Margrave* does not show a reaction that is similar to the reaction as taught in *Tour***" (emphasis added). April 6, 2010 Office Action at page 9.

As an initial point, Appellants question how, if *Margrave* teaches a reaction that is not similar to that of *Tour* or that presently claimed by Appellants, is the citation of *Margrave* as referenced by *Tour* even germane to the present rejection? Clearly, if *Margrave* teaches a reaction that is not similar to that of *Tour* or that presently claimed by Appellants, then the teachings of *Margrave* as referenced by *Tour* are not germane to the present claim rejections. At a minimum, the Examiner's express admission regarding the reaction of *Margrave/Tour* provides cause for withdrawal of the present rejections, since the Examiner has therefore failed to present a *prima facie* showing that the cited references teach or suggest all of the present claim limitations.

Appellants now provide further arguments for the Board demonstrating that the teachings of *Margrave* as referenced by *Tour* do not suggest the presently claimed invention. Appellants provide this showing by way of reference to Appellants' Figure 1 and discussion that follows hereinafter.

As shown in Appellants' Figure 1, a sidewall fluorinated carbon nanotube may react with

an alkyl lithium reagent via a **nucleophilic substitution reaction** mechanism, whereby an alkyl group R from the alkyl lithium reagent is an incoming nucleophile and fluorine from the carbon nanotube is ejected as a fluoride ion leaving group. The lithium ion from the alkyl lithium reagent is a spectator ion that **does not** participate in the reaction or otherwise become covalently bonded to the carbon nanotube. As shown in Appellants' Figure 1, no formal charges form on the carbon nanotube during the concerted process of bond-breaking/bond-making, and there is no discrete, isolable reactive intermediate formed. Similar arguments hold for a putative reaction of fluorinated carbon nanotubes with a Grignard reagent (e.g., R-MgX, where X is a halide), where alkyl group R is again a nucleophile and Mg and X are spectator ions that **do not** participate in the reaction or otherwise become covalently bonded to the carbon nanotube.

As alleged by the Examiner in the April 6, 2010 Office Action at page 4, the teachings of *Tour/Margrave* show that halogenated carbon nanotubes can participate in reactions with an alkyl lithium reagent via a Grignard reaction mechanism. As discussed above and shown in Appellants' Figure 1, the teachings of *Tour/Margrave* clearly show a **nucleophilic substitution reaction**, not a Grignard reaction mechanism. At most the teachings of *Margrave* and *Tour* show that a halogenated carbon nanotube can react with a strong nucleophile (e.g., an alkyl lithium reagent or a Grignard reagent).

Even to the extent that *Tour/Margrave* may teach a reaction of carbon nanotubes with an alkyl lithium reagent, such a **nucleophilic substitution reaction** does not constitute a Grignard reaction mechanism. Such a **nucleophilic substitution reaction** does not result in a metal becoming covalently bonded to the carbon nanotubes (see Appellants' Figure 1), as required by the present claims. Appellants respectfully assert that the referenced teachings of *Tour/Margrave* are fundamentally different than the presently claimed reactions in that the teachings of *Tour/Margrave* **produce different reactive intermediates and products than those presently claimed**. Specifically, Appellants' Figure 2 clearly illustrates a **claimed** reaction in which an aryl-lithium species or an aryl-metal species forms as a reactive intermediate which then reacts with a monomer by anionic polymerization or ring-opening polymerization to produce a polymer-carbon nanotube material in which the polymer is covalently bound to the carbon nanotubes. Although *Tour* does teach a number of polymerization processes including anionic polymerization and ring-opening polymerization (see *Tour*, page 22, line 4), *Tour* alone or in

combination with *Lamb* fails to teach or suggest the claimed feature of forming an aryl-lithium or aryl-metal covalent bond to the carbon nanotubes in order to initiate such a polymerization reaction.

In summary, neither *Tour* nor *Margrave* teach or suggest forming a polymerizable species containing aryl-lithium or aryl-metal covalent bonds on a carbon nanotube. Accordingly, neither reference teaches or suggests forming a polymer therefrom by anionic polymerization or ring-opening polymerization. As discussed hereinafter, *Lamb* fails to rectify the deficiencies of *Tour* in that *Lamb* also fails to teach or suggest a polymerizable species containing aryl-lithium or aryl-metal covalent bonds on a carbon nanotube.

VII.3.2 Lamb Fails To Teach or Suggest Initiating a Polymerization Reaction With a Grignard Reagent

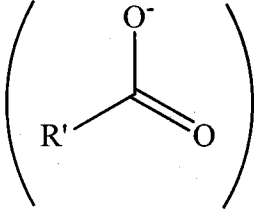
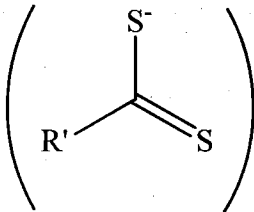
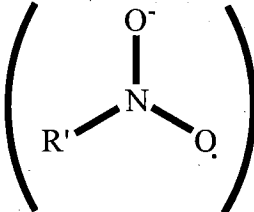
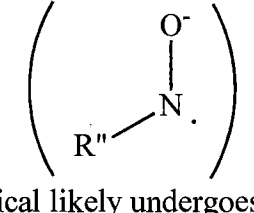
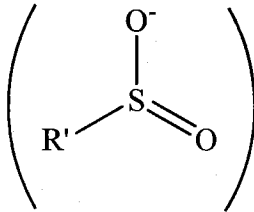
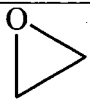
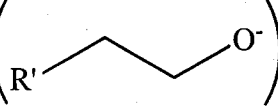
Appellants now show that *Lamb* also does not teach or suggest a polymerizable species containing aryl-lithium or aryl-metal covalent bonds to a carbon nanotube or formation of a polymer therefrom. In other words, *Lamb* also does not teach or suggest a Grignard reaction mechanism for initiating a polymerization reaction.

Lamb clearly teaches a **Grignard complex** mounted on a solid support that is used to initiate a polymerization process (see *Lamb*, Abstract and Col. 2, lines 1 – 6. *Lamb* teaches that the **Grignard complex** has a formula $RXMg(hal)$ where (hal) is a halogen and X is oxygen, sulfur, selenium or tellurium. *Lamb* teaches that such a **Grignard complex** is formed by the reaction of a **Grignard reagent** $[R'Mg(hal)]$ with an olefinic oxide or a compound containing an unsaturated linkage such as, nitriles, nitroso compounds, aldehydes, ketones, esters and inorganic compounds (e.g., carbon dioxide, carbon disulfide, nitrogen dioxide, nitric oxide, sulfur dioxide). Table 1 below shows the structural formulas of **Grignard complexes** formed from the aforementioned compounds in comparison to those of the parent Grignard reagent. For the **Grignard complexes** shown in Table 1, Appellants have presented the **Grignard complex** structural formulas in an expanded format to include full structural details of the taught structure in order to better distinguish the **Grignard complex** structure from that of the parent **Grignard reagent** structure. For presumable purposes of brevity, the **Grignard complex** structural

formulas taught in *Lamb* are presented in a condensed format of $\text{RXMg}(\text{hal})$, where R is an organic fragment comprising R' originating from the Grignard reagent and R'' originating from the olefinic oxide or compound containing an unsaturated linkage. In Table 1, covalent bonds in the **Grignard complexes** are indicated with a solid line, and formal charges are indicated where appropriate.

Table 1: Grignard Complexes Taught by *Lamb*

Parent Compound Name	Formula of Parent Compound	Formula of Grignard Reagent	Structural Formula of Grignard Complex or Grignard Reagent
-----	-----	$\text{R}'\text{Mg}(\text{hal})$	$(\text{R}'\text{---Mg})^+ \text{X}^-$ (Grignard Reagent)
nitrile	$\text{R}''\text{CN}$	$\text{R}'\text{Mg}(\text{hal})$	$\left(\begin{array}{c} \text{N}^- \\ \\ \text{R}''\text{---C---R}' \end{array} \right) \text{Mg}^{2+}\text{X}^-$
nitroso compound	$\text{R}''\text{NO}$	$\text{R}'\text{Mg}(\text{hal})$	$\left(\begin{array}{c} \text{O}^- \\ \\ \text{R}''\text{---N---R}' \end{array} \right) \text{Mg}^{2+}\text{X}^-$
aldehyde	$\text{R}''(\text{CO})\text{H}$	$\text{R}'\text{Mg}(\text{hal})$	$\left(\begin{array}{c} \text{O}^- \\ \\ \text{R}''\text{---CH---R}' \end{array} \right) \text{Mg}^{2+}\text{X}^-$
ketone	$\text{R}''(\text{CO})\text{R}'''$	$\text{R}'\text{Mg}(\text{hal})$	$\left(\begin{array}{c} \text{O}^- \\ \\ \text{R}''\text{---C---R}' \\ \\ \text{R}''' \end{array} \right) \text{Mg}^{2+}\text{X}^-$
ester	$\text{R}(\text{CO})\text{OR}'''$	$\text{R}'\text{Mg}(\text{hal})$	$(\text{R}'''\text{---O}^-) \text{Mg}^{2+}\text{X}^-$

Parent Compound Name	Formula of Parent Compound	Formula of Grignard Reagent	Structural Formula of Grignard Complex or Grignard Reagent
carbon dioxide	CO ₂	R'Mg(hal)	
carbon disulfide	CS ₂	R'Mg(hal)	
nitrogen dioxide	NO ₂	R'Mg(hal)	 <p>(radical likely undergoes dimerization)</p>
nitric oxide	NO	R'Mg(hal)	 <p>(radical likely undergoes dimerization)</p>
sulfur dioxide	SO ₂	R'Mg(hal)	
olefinic oxide	 e.g.	R'Mg(hal)	

Lamb in no manner teaches or suggests that a Grignard reagent alone may be used to initiate an anionic or ring-opening polymerization process. As taught in *Lamb* and shown in Table 1 above, a Grignard reagent is typically shown as having a formula $R'Mg(hal)$, which **has a covalent bond** between the R' group and the magnesium metal. Grignard reagents are organometallic compounds. In contrast, the Grignard complexes of *Lamb* have completely different structures that do not have a covalent bond between a metal and the R' group. The Grignard complexes of *Lamb* are simple salts having a magnesium cation and mixed anions from the halide of the parent Grignard reagent and the organic addition product of the Grignard reagent with an olefinic oxide or compound containing an unsaturated linkage. The only similarity between the two structures is that in both cases (hal) is a simple anion that maintains charge balance. Since the Grignard complexes of *Lamb* **do not contain a covalent bond** to magnesium, they do not teach or suggest the claim limitation of a polymerizable species having an aryl-lithium or aryl-metal covalent bond.

In addition to the foregoing, *Lamb* clearly demonstrates that initiating a polymerization reaction with a Grignard reagent alone is not taught or suggested according to express disclosure therein. Specifically, the Examples of *Lamb* (see *Lamb*; Col. 4, lines 15 – 66) clearly set forth deposition of a Grignard complex on a stationary phase by first reacting a Grignard reagent with air (Example 1) or sulfur dioxide (Example 2). In either case, the Grignard reagent is completely consumed to form the Grignard complex. Accordingly, there is no Grignard reagent remaining when a monomer is subsequently added to initiate a polymerization reaction. Therefore, *Lamb* cannot teach a Grignard reaction for initiating a polymerization reaction, since formation of the Grignard complex precludes any possibility of a Grignard reagent alone initiating the polymerization reaction.

VII.4 Independent Claim 2

In view of the above comments regarding *Tour* and *Lamb*, Appellants respectfully assert that the cited references in combination fail to teach or suggest all of the limitations of independent claim 2. Specifically, Appellants respectfully assert that the cited references in combination fail to teach or suggest formation of a polymerizable species on the carbon nanotubes comprising aryl-lithium covalent bonds.

As noted above, although *Tour* may teach aryl halide functionalized carbon nanotubes, this reference fails to teach or suggest the claim requirement of an alkyl lithium species reacting with the aryl halide functionalized carbon nanotubes to form a polymerizable species comprising aryl-lithium covalent bonds. *Tour* is silent regarding formation of aryl-lithium covalent bonds on carbon nanotubes starting from aryl halide functionalized carbon nanotubes. *Margrave* fails to rectify the deficiency of *Tour*, since the nucleophilic substitution reaction of *Margrave* also does not result in formation of aryl-lithium covalent bonds on the carbon nanotubes (see Appellants' Figure 1). Finally, *Lamb* does not teach or suggest the claim limitation, since *Lamb* expressly teaches a Grignard complex, not a Grignard reagent for initiating a polymerization process. As noted above, the Grignard complexes of *Lamb* are simple salt structures that do not teach or suggest aryl-lithium covalent bonds.

Further to the above remarks, claim 2 requires initiating an anionic or ring-opening polymerization reaction between a monomer and the polymerizable species to form a polymer-carbon nanotube material having the polymer covalently bound to the carbon nanotubes. As noted above, the cited references in combination fail to teach or suggest the claimed features of the polymerizable species. However, even if the Grignard complex of *Lamb* was combined in some manner with the teachings of *Tour*, one would still not arrive at the claimed invention for the following reasons:

First, *Lamb* expressly describes the Grignard complex as a polymerization catalyst (see *Lamb*, Abstract). The American Heritage Dictionary of the English Language, 4th Edition, Houghton-Mifflin, 2009 defines a catalyst as “a substance, usually used in small amounts relative to the reactants, that modifies and increases the rate of a reaction without being consumed in the process” (emphasis added). Even if one were to combine the Grignard complex of *Lamb* with the aryl halide functionalized carbon nanotubes of *Tour*, the combined invention would not meet the present claim limitations, since a monomer **would not react** with the Grignard complex. Since the Grignard complex of *Lamb* is merely a catalyst, it would only modify the reaction pathway and not itself be consumed in the process. Stated another way, the Grignard complex of *Lamb* is not itself a polymerizable species, much less a polymerizable species meeting the present claim limitations.

Furthermore, since the Grignard complex of *Lamb* is not itself polymerizable, it follows that the Grignard complex of *Lamb* would be incapable of forming a polymer-carbon nanotube material having the polymer covalently bound to the carbon nanotubes, as required by the present claims. At most, combining the Grignard complex of *Lamb* with *Tour* would produce a polymer not covalently bound to the carbon nanotubes. This would be true even if the Grignard complex was covalently attached to the carbon nanotube itself.

In view of the foregoing remarks, Appellants respectfully assert independent claim 2 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.5 *Independent Claim 3*

Regarding independent claim 3, Appellants respectfully assert that this claim is patentable over *Tour* and *Lamb* for at least the same reasons that independent claim 2 is patentable. Appellants' remarks from above are reiterated *in toto*. Specifically, *Tour* and *Lamb* fail to teach or suggest the claimed limitation a metal reacting with aryl halide functionalized carbon nanotubes to form a polymerizable species comprising aryl-metal covalent bonds. As further discussed above, even if the Grignard complex of *Lamb* was combined with *Tour* in some manner, the claimed invention would not result for the following reasons: First, the Grignard complex of *Lamb* is a catalyst that is not itself polymerizable. Second, the Grignard complex of *Lamb* would accordingly fail to produce a polymer that is covalently bound to the carbon nanotubes.

In view of the foregoing remarks, Appellants respectfully assert independent claim 3 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.6 *Independent Claim 10*

In view of the comments hereinabove regarding *Tour* and *Lamb*, Appellants respectfully assert that the cited references in combination also fail to teach or suggest all limitations of independent claim 10. Specifically, Appellants respectfully assert that the cited references fail to

teach or suggest **addition of a deprotonating agent or deprotonation of nucleation sites to form initiator groups** as required by the claim.

Appellants respectfully assert that *Lamb* is completely silent regarding a deprotonation process. At most, *Lamb* teaches a reaction of a Grignard reagent with an olefinic oxide or compound containing an unsaturated linkage to form a **Grignard complex** polymerization catalyst. As clearly shown hereinabove, such formation of a **Grignard complex** does **not** involve a deprotonation.

Given *Lamb*'s silence on deprotonation, the merits of the rejection must stand upon *Tour* alone. However, Appellants respectfully assert that *Tour* also fails to teach or suggest the requisite claim limitations. In the April 6, 2010 Office Action at page 5, the Examiner alleged that the feature of being "operable for anionic or ring opening polymerization" was an inherent feature of *Tour*. Although *Tour* may teach derivatized carbon nanotubes that one might conceptualize of becoming deprotonated, *Tour* fails to teach or suggest the required addition of a deprotonating agent, or, more particularly, *Tour* fails to teach or suggest the deprotonation of nucleation sites to form initiator groups. Hence, the alleged inherency feature of *Tour* in regard to claim 10 is irrelevant, and *Tour* alone fails to teach or suggest the required claim limitations. Furthermore, the teachings of *Margrave* as referenced by *Tour* fail to teach or suggest the claimed deprotonation to form initiator groups (see Appellants' Figure 1). In summary, although *Tour* may teach a number of polymerization processes, including anionic polymerization and ring-opening polymerization, this reference fails to teach or suggest formation of initiator groups for initiating a polymerization reaction.

In view of the foregoing remarks, Appellants respectfully assert that independent claim 10 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7 Dependent Claims 4 – 6, 8, 9, 11 – 28 and 31 – 34

VII.7.1 Claim 4

Claim 4 incorporates all of the patentable limitations of claim 3 and further recites that

the metal is selected from zinc, nickel, potassium, sodium, lithium, magnesium, cesium, palladium and combinations thereof. Therefore, claim 4 is patentable for at least the same reasons that claim 3 is patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 4 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.2 Claim 5

Claim 5 incorporates all of the patentable limitations of claim 3 and further recites that the metal is Mg, where the aryl-metal bonds are aryl-Mg bonds comprising a Grignard species. Therefore, claim 5 is patentable for at least the same reasons that claim 3 is patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 5 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.3 Claim 6

Claim 6 incorporates all of the patentable limitations of any one of claims 2 – 5 and further recites that the aryl halides are bonded to a sidewall of the aryl halide functionalized carbon nanotubes. Therefore, claim 6 is patentable for at least the same reasons that claims 2 and 3 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 6 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.4 Claim 8

Claim 8 incorporates all of the patentable limitations of any one of claims 2 – 5 and further recites that the aryl halide is an aryl bromide. Therefore, claim 8 is patentable for at least the same reasons that claims 2 and 3 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 8 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.5 Claim 9

Claim 9 incorporates all of the patentable limitations of claim 2 and further recites that

the alkyllithium species is n-butyllithium. Therefore, claim 9 is patentable for at least the same reasons that claim 2 is patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 9 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.6 Claim 11

Claim 11 incorporates all of the patentable limitations of claim 10 and further recites that the nucleation sites comprise at least one element selected from carbon, sulfur, oxygen and nitrogen. Therefore, claim 11 is patentable for at least the same reasons that claim 10 is patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 11 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.7 Claim 12

Claim 12 incorporates all of the patentable limitations of claim 10 and further recites that the functionalized carbon nanotubes are selected from phenol functionalized carbon nanotubes, thiophenol functionalized carbon nanotubes, phenethyl alcohol functionalized carbon nanotubes (CNT-C₆H₄-CH₂CH₂OH), CNT-C₆H₄-NHBoc, and combinations thereof. Therefore, claim 12 is patentable for at least the same reasons that claim 10 is patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 12 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.8 Claim 13

Claim 13 incorporates all of the patentable limitations of any one of claims 10 – 12 and further recites that the nucleation sites are on the sidewall of the functionalized carbon nanotubes. Therefore, claim 13 is patentable for at least the same reasons that claim 10 is patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 13 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.9 Claim 14

Claim 14 incorporates all of the patentable limitations of any one of claims 10 – 12 and further recites that the deprotonating agent comprises a base. Therefore, claim 14 is patentable for at least the same reasons that claim 10 is patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 14 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.10 Claim 15

Claim 15 incorporates all of the patentable limitations of claim 14 and further recites that the base is selected from KOH, KH, NaOH, NaH and potassium hexamethyldisilazide. Therefore, claim 15 is patentable for at least the same reasons that claim 10 is patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 15 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.11 Claim 16

Claim 16 incorporates all of the patentable limitations of any one of claims 10 – 12 and further recites that the deprotonating agent comprises a metal operable for deprotonating nucleation sites. Therefore, claim 16 is patentable for at least the same reasons that claim 10 is patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 16 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.12 Claim 17

Claim 17 incorporates all of the patentable limitations of claim 16 and further recites that the metal is selected from zinc, nickel, potassium, sodium, lithium, magnesium, cesium, palladium and combinations thereof. Therefore, claim 17 is patentable for at least the same reasons that claim 10 is patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 17 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.13 Claim 18

Claim 18 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that the initiating step comprises initiating anionic polymerization. Therefore, claim 18 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 18 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.14 Claim 19

Claim 19 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that the initiating step comprises ring opening polymerization. Therefore, claim 19 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 19 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.15 Claim 20

Claim 20 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that the functionalized carbon nanotubes are single-wall carbon nanotubes. Therefore, claim 20 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 20 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.16 Claim 21

Claim 21 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that the solvent is tetrahydrofuran. Therefore, claim 21 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 21 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.17 Claim 22

Claim 22 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that the monomer is selected from styrene, acrylates, methyl acrylates, vinyl acetate, vinyl pyridines, isoprene, butadiene, chloroprene, acrylonitrile, maleic anhydride and combinations thereof. Therefore, claim 22 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 22 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.18 Claim 23

Claim 23 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that the monomer comprises styrene. Therefore, claim 23 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 23 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.19 Claim 24

Claim 24 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that the methods further comprise adding a terminating agent suitable for terminating the polymerization reaction. Therefore, claim 24 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 24 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.20 Claim 25

Claim 25 incorporates all of the patentable limitations of claim 24 and further recites that the terminating agent is selected from ethanol, acetaldehyde, trimethylsilyl chloride, and combinations thereof. Therefore, claim 25 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 25 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a)

rejection be withdrawn.

VII.7.21 Claim 26

Claim 26 incorporates all of the patentable limitations of claim 24 and further recites that the terminating agent is ethanol. Therefore, claim 26 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 25 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.22 Claim 27

Claim 27 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that a concentration of the monomer is between about 0.03 and about 0.16 g/mL. Therefore, claim 27 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 27 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.23 Claim 28

Claim 28 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that the initiating step occurs at a temperature between about 0°C and about 50°C. Therefore, claim 28 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 28 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.24 Claim 31

Claim 31 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that the methods further comprise adding a polymerization catalyst to the solvent. Therefore, claim 31 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 31 is

not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.25 Claim 32

Claim 32 incorporates all of the patentable limitations of claim 31 and further recites that the polymerization catalyst comprises TiCl_4 . Therefore, claim 32 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 32 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.26 Claim 33

Claim 33 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that the methods further comprise utilizing the polymer-carbon nanotube material in a drug delivery process. Therefore, claim 33 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 33 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VII.7.27 Claim 34

Claim 34 incorporates all of the patentable limitations of any one of claims 2 – 5 or 10 – 12 and further recites that the methods further comprise utilizing the polymer-carbon nanotube material for scaffolding to promote cellular growth. Therefore, claim 34 is patentable for at least the same reasons that claims 2, 3 and 10 are patentable. In view of the foregoing remarks, Appellants respectfully assert that claim 34 is not obvious in view of *Tour* and *Lamb* and request that the 35 U.S.C. § 103(a) rejection be withdrawn.

VIII. CONCLUSION

For at least the reasons noted above, Appellants respectfully assert that the Examiner's rejections of claim 2 – 6, 8 – 28 and 31 – 34 are in error and request that the Examiner's decision be reversed.

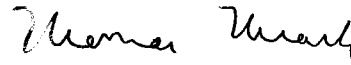
Respectfully submitted,

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IX. CLAIMS APPENDIX

2. A method comprising:

- a) providing aryl halide functionalized carbon nanotubes;
wherein the aryl halide comprises a halide selected from the group consisting of chlorine, bromine, iodine, and combinations thereof;
- b) dispersing the aryl halide functionalized carbon nanotubes in a solvent;
- c) adding an alkyllithium species to the solvent,
wherein the alkyllithium species reacts with the aryl halide functionalized carbon nanotubes to form an aryl-lithium species;
wherein the aryl-lithium species comprises a polymerizable species on the carbon nanotubes; and
wherein the polymerizable species comprises aryl-lithium covalent bonds;
- d) adding a monomer to the solvent; and
- e) initiating a polymerization reaction between the monomer and the polymerizable species to form a polymer-carbon nanotube material,
wherein a polymer comprising the polymer-carbon nanotube material is covalently bound to the carbon nanotubes; and
wherein the polymerization reaction is selected from the group consisting of anionic polymerization and ring opening polymerization.

3. A method comprising:

- a) providing aryl halide functionalized carbon nanotubes;
wherein the aryl halide comprises a halide selected from the group consisting of chlorine, bromine, iodine, and combinations thereof;
- b) dispersing the aryl halide functionalized carbon nanotubes in a solvent;
- c) adding a metal to the solvent,
wherein the metal reacts with the aryl halide functionalized carbon nanotubes to form an aryl-metal species;
wherein the aryl-metal species comprises a polymerizable species on the carbon nanotubes; and

wherein the polymerizable species comprises aryl-metal covalent bonds;

- d) adding a monomer to the solvent; and
- e) initiating a polymerization reaction between the monomer and the polymerizable species to form a polymer-carbon nanotube material,

wherein a polymer comprising the polymer-carbon nanotube material is covalently bound to the carbon nanotubes; and

wherein the polymerization reaction is selected from the group consisting of anionic polymerization and ring opening polymerization.

4. The method of Claim 3, wherein the metal is selected from the group consisting of zinc, nickel, potassium, sodium, lithium, magnesium, cesium, palladium, and combinations thereof.
5. The method of Claim 3, wherein the metal is Mg,
wherein the aryl-metal bonds are aryl-Mg bonds comprising a Grignard species.
6. The method of any one of Claims 2 – 5, wherein the aryl halides are bonded to the sidewall of the aryl halide functionalized carbon nanotubes.
8. The method of any one of Claims 2 – 5, wherein the aryl halide is an aryl bromide.
9. The method of Claim 2, wherein the alkyllithium species is n-butyllithium.
10. A method comprising:
 - a) providing functionalized carbon nanotubes,
wherein the functionalized carbon nanotubes comprise nucleation sites operable for initiating a polymerization reaction after deprotonation of said nucleation sites to form initiator groups;
wherein the polymerization reaction is selected from the group consisting of anionic polymerization and ring opening polymerization;
 - b) dispersing the functionalized carbon nanotubes in a solvent;
 - c) adding a deprotonating agent to the solvent,

wherein the deprotonating agent deprotonates the nucleation sites to form initiator groups operable for initiating the polymerization reaction;

- d) adding a monomer to the solvent; and
- e) initiating a polymerization reaction between the monomer and the initiator groups to form a polymer-carbon nanotube material,

wherein a polymer comprising the polymer-carbon nanotube material is covalently bound to the carbon nanotubes; and

wherein the polymerization reaction is selected from the group consisting of anionic polymerization and ring opening polymerization.

11. The method of Claim 10, wherein the nucleation sites comprise at least one element selected from the group consisting of carbon, sulfur, oxygen, and nitrogen.
12. The method of Claim 10, wherein the functionalized carbon nanotubes are selected from the group consisting of phenol functionalized carbon nanotubes, thiophenol functionalized carbon nanotubes, phenethyl alcohol functionalized nanotubes (CNT-C₆H₄-CH₂CH₂OH), CNT-C₆H₄-NHBoc, and combinations thereof.
13. The method of any one of Claims 10 – 12, wherein the nucleation sites are on the sidewall of the functionalized carbon nanotubes.
14. The method of any one of Claims 10 – 12, wherein the deprotonating agent comprises a base.
15. The method of Claim 14, wherein the base is selected from the group consisting of KOH, KH, NaOH, NaH, and potassium hexamethyldisilazide.
16. The method of any one of Claims 10 – 12, wherein the deprotonating agent comprises a metal operable for deprotonating the nucleation sites.
17. The method of Claim 16, wherein the metal is selected from the group consisting of zinc, nickel, potassium, sodium, lithium, magnesium, cesium, palladium, and combinations thereof.

18. The method of any one of Claims 2 – 5 or 10 – 12, wherein the initiating step comprises initiating anionic polymerization.
19. The method of any one of Claims 2 – 5 or 10 – 12, wherein the initiating step comprises initiating ring opening polymerization.
20. The method of any one of Claims 2 – 5 or 10 – 12, wherein the functionalized carbon nanotubes are single-wall carbon nanotubes.
21. The method of any one of Claims 2 – 5 or 10 – 12, wherein the solvent is tetrahydrofuran.
22. The method of any one of Claims 2 – 5 or 10 – 12, wherein the monomer is selected from the group consisting of styrene, acrylates, methyl acrylates, vinyl acetate, vinyl pyridines, isoprene, butadiene, chloroprene, acrylonitrile, maleic anhydride, and combinations thereof.
23. The method of any one of Claims 2 – 5 or 10 – 12, wherein the monomer comprises styrene.
24. The method of any one of Claims 2 – 5 or 10 – 12, further comprising adding a terminating agent suitable for terminating the polymerization reaction.
25. The method of Claim 24, wherein the terminating agent is selected from the group consisting of ethanol, acetaldehyde, trimethylsilyl chloride, and combinations thereof.
26. The method of Claim 24, wherein the terminating agent is ethanol.
27. The method of any one of Claims 2 – 5 or 10 – 12, wherein a concentration of the monomer is between about 0.03 and about 0.16 g/ml.
28. The method of any one of Claims 2 – 5 or 10 – 12, wherein the initiating step occurs at a temperature between about 0°C and about 50°C.
31. The method of any one of Claims 2 – 5 or 10 – 12, further comprising adding a polymerization catalyst to the solvent.

32. The method of Claim 31, wherein the polymerization catalyst comprises TiCl_4 .
33. The method of any one of Claims 2 – 5 or 10 – 12, further comprising a step of utilizing the polymer-carbon nanotube material in a drug delivery process.
34. The method of any one of Claims 2 – 5 or 10 – 12, further comprising a step of utilizing the polymer-carbon nanotube material for scaffolding to promote cellular tissue growth.

X. EVIDENCE APPENDIX

As evidence for this appeal, Appellants rely on the following references, which are submitted as exhibits with this appeal brief:

- 1) International Patent Application Publication WO 02/060812 (*Tour*);
- 2) United States Patent 3,554,992 (*Lamb*);
- 3) Final Office Action mailed April 6, 2010; and
- 4) United States Patent 6,827,918 (hereinafter, *Margrave*).

XI. RELATED PROCEEDINGS APPENDIX

None.

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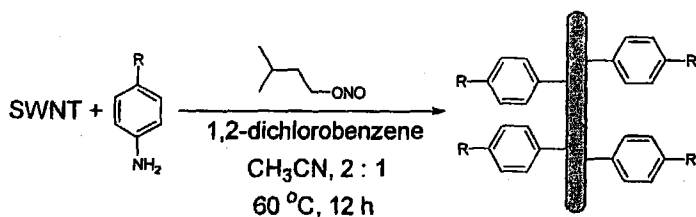
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(54) Title: PROCESS FOR DERIVATIZING CARBON NANOTUBES WITH DIAZONIUM SPECIES AND COMPOSITIONS THEREOF



16, R = Cl

17, R = *tert*-butyl18, R = CO₂CH₃19, R = NO₂

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21, R = CCCCCCCCCCCCCCCC(=O)O(57) Abstract: The invention incorporates new processes for the chemical modification of carbon nanotubes. Such processes involve the derivatization of multi- and single-wall carbon nanotubes, including small diameter (*ca.* 0.7 nm) single-wall carbon nanotubes, with diazonium species. The method allows the chemical attachment of a variety of organic compounds to the side and ends of carbon nanotubes. These chemically modified nanotubes have applications in polymer composite materials, molecular electronic applications and sensor devices. The methods of derivatization include electrochemical induced reactions thermally induced reactions (via *in-situ* generation of diazonium compounds or pre-formed diazonium compounds), and photochemically induced reactions. The derivatization causes significant changes in the spectroscopic properties of the

nanotubes. The estimated degree of functionality is *ca.* 1 out of every 20 to 30 carbons in a nanotube bearing a functionality moiety. Such electrochemical reduction processes can be adapted to apply site-selective chemical functionalization of nanotubes. Moreover, when modified with suitable chemical groups, the derivatized nanotubes are chemically compatible with a polymer matrix, allowing transfer of the properties of the nanotubes (such as, mechanical strength or electrical conductivity) to the properties of the composite material as a whole. Furthermore, when modified with suitable chemical groups, the groups can be polymerized



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PROCESS FOR DERIVATIZING CARBON NANOTUBES WITH DIAZONIUM SPECIES AND COMPOSITIONS THEREOF

The present invention was made in connection with research pursuant to grant numbers NASA-JSC-NCC 9-77 from the National Aeronautics and Space Administration; grant number NSR-DMR-0073046 from the National Science Foundation; and grant number N00014-99-1-0406 from the DARPA/ONR.

FIELD OF INVENTION

The present invention relates broadly to carbon nanotubes. More specifically, the invention relates to derivatization of carbon nanotubes with diazonium compounds and to uses for the derivatized carbon nanotubes.

BACKGROUND OF THE INVENTION

Fullerenes are closed-cage molecules composed entirely of sp^2 -hybridized carbons, arranged in hexagons and pentagons. Fullerenes (e.g., C_{60}) were first identified as closed spheroidal cages produced by condensation from vaporized carbon. Fullerene tubes are produced in carbon deposits on the cathode in carbon arc methods of producing spheroidal fullerenes from vaporized carbon. Ebbesen *et al.* (Ebbesen I), "Large-Scale Synthesis Of Carbon Nanotubes," *Nature*, Vol. 358, p. 220 (July 16, 1992) and Ebbesen *et al.*, (Ebbesen II), "Carbon Nanotubes," *Annual Review of Materials Science*, Vol. 24, p. 235 (1994). Such tubes are referred to herein as carbon nanotubes. Many of the carbon nanotubes made by these processes were multi-wall nanotubes, i.e., the carbon nanotubes resembled concentric cylinders. Carbon nanotubes having up to seven walls have been described in the prior art. Ebbesen II; Iijima *et al.*, "Helical Microtubules Of Graphitic Carbon," *Nature*, Vol. 354, p. 56 (November 7, 1991).

Since 1991, there has been a great deal of interest in derivatization of carbon nanotubes, and more, particularly, single-wall carbon nanotubes, to facilitate their manipulation, to enhance the solubility of such nanotubes, and to make the nanotubes more amenable to composite formation. This is because single-wall carbon nanotubes are one of the more striking discoveries in the chemistry and materials genre in recent years. Nanotubes possess tremendous strength, an extreme aspect ratio, and are excellent thermal and electrical conductors. A plethora of potential applications for nanotubes have been hypothesized, and some progress is being made towards commercial applications. Accordingly, chemical modification of single-wall carbon nanotubes, as well as multi-wall carbon nanotubes, will be necessary for some applications. For instance, such applications may require grafting of moieties to the nanotubes: to allow assembly of modified nanotubes, such as single-wall carbon nanotubes, onto surfaces for electronics applications; to allow reaction with host matrices in composites; and to allow the presence of a variety of functional groups bound to the nanotubes, such as single-wall carbon nanotubes, for sensing applications.

While there have been many reports and review articles on the production and physical properties of carbon nanotubes, reports on chemical manipulation of nanotubes have been slow to emerge. There have been reports of functionalizing nanotube ends with carboxylic groups (Rao, *et al.*, *Chem. Commun.*, 1996, 1525-1526; Wong, *et al.*, *Nature*, 1998, 394:52-55), and then further

manipulation to tether them to gold particles via thiol linkages (Liu, *et al.*, *Science*, 1998, 280:1253-1256). Haddon and co-workers (Chen, *et al.*, *Science*, 1998, 282:95-98) have reported solvating single-wall carbon nanotubes by adding octadecylamine groups on the ends of the tubes and then adding dichlorocarbenes to the nanotube sidewall, albeit in relatively low quantities (~2%).

5 Success at covalent sidewall derivatization of single-wall carbon nanotubes has been limited in scope, and the reactivity of the sidewalls has been compared to the reactivity of the basal plane of graphite. Aihara, J. *J. Phys. Chem.* 1994, 98, 9773-9776. A viable route to direct sidewall functionalization of single-wall carbon nanotubes has been fluorination at elevated temperatures, which process was disclosed in a co-pending application commonly assigned to the assignee of the
10 Application, United States Patent Application Serial No. 09/810,390, "Chemical Derivatization Of Single-Wall Carbon Nanotubes To Facilitate Solvation Thereof; And Use Of Derivatized Nanotubes To Form Catalyst-Containing Seed Materials For Use In Making Carbon Fibers," to Margraves *et al.*, filed March 16, 2001. These functionalized nanotubes may either be de-fluorinated by treatment with hydrazine or allowed to react with strong nucleophiles, such as alkyllithium reagents. Although
15 fluorinated nanotubes may well provide access to a variety of functionalized materials, the two-step protocol and functional group intolerance to organolithium reagents may render such processes incompatible with certain, ultimate uses of the carbon nanotubes. Other attempts at sidewall modification have been hampered by the presence of significant graphitic or amorphous carbon contaminants. Chen, Y. *et al.*, *J. Mater Res.* 1998 13, 2423-2431.

20 It would thus be desirable to develop a direct approach to high degrees of functionalization of nanotubes that would be accommodating (*i.e.* a one step approach and one that is compatible with certain, ultimate uses of the nanotubes). Such uses include applications to utilize the tremendous strength, extreme aspect ratios, and excellent thermal and electrical conductive properties of the nanotubes.

25 Accordingly, it is an object of this invention to provide a method for derivatizing carbon nanotubes, especially the sidewalls and end-caps of single-wall carbon nanotubes, utilizing chemistries that are direct, accommodating, and compatible with the ultimate uses and applications of the nanotubes.

SUMMARY OF THE INVENTION

30 The invention incorporates new processes for the chemical modification of carbon nanotubes. Such processes involve the derivatization of multi- and single-wall carbon nanotubes, including small diameter (*ca.* 0.7 nm) single-wall carbon nanotubes, with diazonium species. The method allows the chemical attachment of a variety of organic compounds to the side and ends of carbon nanotubes. These chemically modified nanotubes have applications in polymer composites,
35 molecular electronic applications, and sensor devices. The methods of derivatization include electrochemical induced reactions, thermally induced reactions (*via in-situ* generation of diazonium compounds or *via* preformed diazonium compounds), and photochemically induced reactions. The derivatization causes significant changes in the spectroscopic properties of the nanotubes. The

estimated degree of functionality is ca. 1 out of every 20 to 30 carbons in a nanotube bearing a functionality moiety.

5 The electrochemical induced processes include procedures utilizing an assembly of nanotubes, such as a piece of "bucky paper" or mat, which can be held with a silver paste covered alligator clip and immersed in an acetonitrile solution of a diazonium salt and a supporting electrolyte salt, while applying a potential (typically a negative potential) to the assembly of nanotubes. By such a process, a molecular wire (such as an oligo(phenylene ethynylene) molecular wire) and also a molecular electronic device have been covalently attached to a nanotube. This represents the marriage of wire-like nanotubes with molecular wires and with molecular electronic devices.

10 Such electrochemical processes can be adapted to apply site-selective chemical functionalization of nanotubes. Moreover, it allows for the controlled attachment of two or more different chemical functionalities to different locations on the nanotubes.

15 The thermally induced processes include procedures in which a dispersion of carbon nanotubes in an organic solvent mixture is treated with a precursor to a reactive diazonium species. This precursor is then transformed *in-situ* to the reactive species, and its thermal decomposition leads to chemical attachment to the carbon nanotubes. It is believed that such a process has the advantage of scalability and avoids the necessity of isolating and storing potentially unstable diazonium compounds, *i.e.*, the species that reacts with the carbon nanotubes.

20 Moreover, the thermal induced processes also include procedures utilizing pre-formed diazonium species. The reactive species can be prepared beforehand, isolated, and added to the mixture. Additional variations include variations in the temperature of the process (ambient temperature and higher and lower temperatures), ratio of reactants, and a variety of organic solvents.

25 The photochemical induced processes are similar to the thermal induced reaction except that a photochemical process (not a thermal process) is utilized to cause the decomposition of the diazonium species that leads to the chemical attachment of the moieties to the carbon nanotubes.

30 When modified with suitable chemical groups, the nanotubes are chemically compatible with a polymer matrix, allowing transfer of the properties of the nanotubes (such as mechanical strength) to the properties of the composite material as a whole. To achieve this, the modified carbon nanotubes can be thoroughly mixed (physically blended) with the polymeric material, and/or, if desired, allowed to react at ambient or elevated temperature. These methods can be utilized to append functionalities to the nanotubes that will further covalently bond to the host polymer matrix, or directly between two tubes themselves.

35 There are a multitude of variations in the chemical structure of the polymer matrix, *i.e.*, polyethylene, various epoxy resins, polypropylene, polycarbonate *etc.* In general, possible composite materials could be made with chemically modified nanotubes and thermoplastics, thermosets, elastomers, and others. There is also a host of variations possible in the chemical groups that can be attached to the nanotubes. The specific group will be chosen to enhance

compatibility with the particular polymer matrix desired and, if desired, to cause chemical bonding to the host material.

Furthermore, when modified with suitable chemical groups, the nanotubes can be used as a generator of polymer growth. *I.e.*, the nanotubes would be derivatized with a functional group that could be an active part of a polymerization process, which would also result in a composite material in which the carbon nanotubes are chemically involved.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 shows the structure of certain aryl diazonium salts used to derivatize single-wall carbon nanotubes.

FIGURE 2 shows the scheme utilized to prepare Compounds **9** and **11** as reflected in Figure 1.

FIGURE 3 shows the absorption spectra in dimethylformamide for (A) **SWNT-p** and (B) **SWNT-1**.

FIGURE 4 shows the absorption spectra in dimethylformamide for (A) **SWNT-p** and (B) **SWNT-8**.

FIGURE 5 shows the Raman spectra from solid samples, with excitation at 782 nm, for (A) **SWNT-p** and (B) **SWNT-1**.

FIGURE 6 shows the Raman spectra in the radial breathing mode region for (A) **SWNT-4** and (B) **SWNT-p**.

FIGURE 7 shows the infrared spectra (attenuated total reflectance) of derivatized nanotubes for (A) **SWNT-4** and (B) **SWNT-6**.

FIGURE 8 shows the thermogravimetric analysis data in argon for **SWNT-10**.

FIGURE 9 shows the Raman spectra for (A) **SWNT-p**, (B) **SWNT-2**, and (C) **SWNT-2** after TGA.

FIGURE 10 shows the high-resolution TEM images for (A) **SWNT-p** and (B) **SWNT-4**. The scale bar applies to both images.

FIGURE 11 shows electrochemical grafting of an aryl diazonium salt onto a carbon surface.

FIGURE 12 shows the reaction sequence for derivatization of single-wall carbon nanotubes by *in-situ* generation of the diazonium species, and examples of functionalized phenyl moieties employed in reactions.

FIGURE 13 shows the absorption spectra in dimethylformamide for (A) **SWNT-p** and (B) **18**. The spectra for **16**, **17**, and **19** are similar, with little or no visible structure. The spectrum of the material from the sequence to produce **20** was essentially equivalent to that shown for **SWNT-p**.

FIGURE 14 shows the Raman spectra from solid samples, with excitation at 782 nm, for (A) **SWNT-p** and (B) **17**. The Raman spectra of **16**, **18**, and **19** are similar, but with differing ratios of the peak intensities. In all these cases, the relative intensity of the disorder mode is increased. The spectrum of the material from the sequence to produce **20** was essentially equivalent to that shown for **SWNT-p**.

FIGURE 15 shows the reaction sequence for photochemical derivatization of a single-wall carbon nanotube.

FIGURE 16 shows an example of the portions comprising an epoxy resin.

FIGURE 17 shows examples of nanotubes that are chemically modified with groups compatible with the curing agent portion, and reactive with the epoxy portion of a thermosetting resin.

FIGURE 18 shows a schematic depiction of carbon nanotube containing composite material where the freehand lines represent the polymer matrix that is cross-linked by the chemically modified carbon nanotubes, creating a thermosetting composite material.

FIGURE 19 shows a depiction of chemically modified carbon nanotubes cross-linked via disulfide linkages.

FIGURE 20 shows the preparation of nanotubes chemically modified with thiophenol moieties.

FIGURE 21 shows the preparation of carbon nanotubes chemically modified with pendant epoxy groups that are compatible with the epoxy portion of a resin and reactive with the curing agent portion of a thermosetting resin, as reflected in FIGURE 16.

FIGURE 22 shows an example of a composite material based on poly(methylmethacrylate) and chemically modified carbon nanotubes, based on a hydrogen bonding motif (indicated by the dashed lines).

FIGURE 23 shows an example of chemically modified nanotubes being used in a polymerization process to grow the polymer from the nanotubes.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

Electrochemical Derivatization of Carbon Nanotubes with Diazonium Species

Aryl diazonium salts are known to react with electron deficient olefins, known as the Meerwein reaction. Obushak, M. D., *et al.*, *Tett. Lett.* 1998, 39, 9567-9570. In such solution phase reactions, diazonium salt decomposition is typically catalyzed by a metal salt such as copper(I) chloride, giving a reactive aryl radical. In some cases, the reaction is believed to proceed through an aryl cation. This type of chemistry has been successfully applied to the modification of carbon surfaces via grafting of electrochemically reduced aryl diazonium salts. Delamar, M., *et al.*, *Carbon* 1997, 35, 801-807; Allongue, P., *et al.*, *J. Am Chem. Soc.* 1997, 119, 201-207; Ortiz, B., *et al.*, *J. Electro. Chem.* 1998, 455, 75-81; Saby, C., *et al.*, *Langmuir* 1997, 13, 6805- 6813; Delamar, M, *et al.*, *J. Am. Chem. Soc.* 1992, 114, 5883-5884. Reduction may give an aryl radical that covalently attaches to the carbon surface. This technique has been applied to both highly ordered pyrolytic graphite (HOPG) and glassy carbon (GC) electrodes.

Methylene chloride and acetonitrile were distilled from calcium hydride. Dimethylformamide was distilled and stored over molecular sieves. Tetrahydrofuran was distilled from sodium/benzophenone ketyl. All other reagents were obtained commercially and used without further purification.

Carbon Nanotubes. A method for producing small diameter (ca. 0.7 nm) single-wall carbon nanotubes has been developed by Smalley, *et al.* Nikolaev, P., *et al.*, *Chem. Phys. Lett.* 1999, 313,

91-97. This method is disclosed in a co-pending application commonly assigned to the assignee of the Application, United States Patent Application Serial No. 09/830,642 "Gas-Phase Nucleation and Growth of Single-Wall Carbon Nanotubes from High Pressure CO," to Smalley *et al.*, filed April 27, 2001, which is incorporated herein by reference. This material is now commercially available (Carbon Nanotechnologies Inc., HiPco material). As the diameter of these nanotubes is approximately the same as that of C₆₀, these nanotubes are understood to display enhanced reactivity relative to the larger diameter tubes typically produced by laser oven methods, since the reactivity of C₆₀ has been attributed in part to curvature strain. While the present invention is also pertinent to multi-wall carbon nanotubes and larger diameter single-wall carbon nanotubes, these small diameter nanotubes were primarily utilized during the examples demonstrating the present process. A variety of diazonium salts have been used, including those that provide moieties conducive to further elaboration after attachment of the nanotubes. Also, an oligo (phenylene ethynylene) molecular device similar to the one that has been shown to exhibit memory and room temperature negative resistance (Chen, J. *et al.*, *App. Phys. Lett.* 2000, 77, 1224-1226) has been attached to the nanotubes.

The following examples, as well as, the other examples described herein, are presented to further illustrate the invention and, are not to be construed as unduly limiting the scope of this invention.

A. Examples Nos. 1-11

For the electrochemical derivatization experiments, a piece of bucky paper, formed by filtration of a suspension, was used as the working electrode in a 3-electrode cell and immersed in an acetonitrile solution containing the diazonium salt and an electrolyte. The diazonium salts were probably reduced to aryl radicals at the surface of the bucky paper, and subsequently become covalently attached to the nanotubes. The conductivity of single-wall carbon nanotubes has been well documented. In general, aryl diazonium salts are easily prepared under conditions that tolerate a variety of functional groups. Consequently, the method described herein allows functionalization of nanotubes with a wide variety of diazonium salts, including those that provide chemical handles for additional elaboration after attachment to nanotubes.

The purified single-wall nanotubes (hereafter, **SWNT-p**) used in this investigation contained little amorphous or other extraneous carbon contaminants. The purification technique for the nanotubes is discussed in more detail below. The fact the **SWNT-p** contained little amorphous or other extraneous carbon contaminants is significant, as the presence of such material may have hindered the ability to determine whether previous derivatization efforts were successful. (While the lack of impurities was an issue in the initial demonstrations respecting the operability of the reactions, it should be noted that these reactions will work on raw, impurified multi- and single-wall carbon nanotubes, *i.e.* the reactions will work even in the absence of a purification process.) In addition, the residual iron content (catalyst from the gas-phase growth technique) was <1 atomic% by electron microprobe analysis (EMPA) (ca. 0.3 atomic %). The diazonium salts used to derivatize **SWNT-p** are shown in Figure 1. Compounds 1-7 and 11 were prepared from the corresponding

aniline derivatives by known methods (Kosynkin, D.; Tour, J. M. *Org. Lett.* 2000), using nitrosonium tetrafluoroborate as the diazotization reagent. Compound **8** was prepared using the process reported in Kosynkin, D., *et al.*, *Org. Lett.* 2001, 3, 993-995. Compound **9** and **10** were prepared according to scheme reflected in Figure 2. Characterization of these compounds is further discussed below. Reaction of these compounds with **SWNT-p** generated **SWNT-x**, where x = **1-9** and **11-12**, respectively.

The small diameter single-wall carbon nanotubes used in this investigation were produced by a gas-phase catalytic technique, using carbon monoxide as the feedstock and iron carbonyl as the catalyst. Nikolaev, P., *et al.*, *Chem. Phys. Lett.* 1999, 313, 91-97; United States Patent Application Serial No. 09/830,642. (These carbon nanotubes are now commercially available; Carbon Nanotechnologies Inc., HiPco material). The raw production material was purified by air oxidation at 150°C for a period of 12 hours, followed by annealing in argon at 800°C for 6 hours. This material was sonicated in concentrated hydrochloric acid (ca. 30 mg in 60 mL), filtered, washed extensively with water and 2-propanol, and dried under vacuum. The purity of these samples was verified by SEM, TEM, and EMPA.

Bucky Paper. The use of bucky paper as a working electrode for the derivatization raises several unique issues. Electrical contact between the source and the bucky paper during the electrochemical process is an issue. This situation can be improved by application of colloidal silver paste to the alligator clip used to hold the bucky paper. It is also believed that the success of the reaction is at least partially dependent on the quality of the bucky paper employed as the working electrode. Accordingly, it was helpful to achieve a suspension that contained little or no visible particulate prior to filtration to form the bucky paper.

General procedure for diazotization of aniline derivatives. A portion of nitrosonium tetrafluoroborate (1.2 molar equivalents) was weighed out in a glove box and sealed. After removal from the glove box, acetonitrile was added (3 mL/mmol of aniline), and the solution was cooled to -30°C. A solution of the aniline derivative (1 molar equivalent) in acetonitrile (ca. 1 mL/mmol) was added dropwise while stirring (vide infra). In some cases, dry methylene chloride was used as a co-solvent for the aniline derivative. After complete addition, stirring was continued for 30 minutes, at which time the cold bath was removed. After stirring for a total of 1 hour, the solution was diluted with a 2x volume of ether and stirred. The precipitate was collected by filtration and washed with ether.

4-Bromobenzenediazonium tetrafluoroborate (1). Yield: 85%. MP 138°C. ¹H NMR (400 MHz, CD₃CN) δ 8.22 (ABq, J = 9.1 Hz, Δv = 102.1 Hz, 4H).

4-Chlorobenzenediazonium tetrafluoroborate (2). Yield: 78%. MP 134°C. ¹H NMR (400 MHz, CD₃CN) δ 8.24 (ABq, J = 9.2 Hz, Δv = 214.2 Hz, 4H).

4-Fluorobenzenediazonium tetrafluoroborate (3). Yield: 79%. MP 160°C. ¹H NMR (400 MHz, CD₃CN) δ 8.64 (dd, J = 9.4 Hz, 9.5 Hz, 2H), 7.69 (dd, J = 9.4 Hz, 9.5 Hz, 2H).

4-tert-Butylbenzenediazonium tetrafluoroborate (4). The 4-tert-butylaniline was dissolved in a 1:1 mixture of acetonitrile and dry methylene chloride prior to addition to the nitrosonium

tetrafluoroborate. Yield: 78%. MP 91°C. IR (KBr) 3364.8, 3107.3, 2968.6, 2277.2, 1579.2, 1482.0, 1418.0, 1373.5, 1269.8, 1056.9, 841.1, 544.6, 621.4 cm⁻¹. ¹H NMR (400 MHz, CD₃CN) δ 8.16 (ABq, J = 9.0 Hz, Δv = 298.7 Hz, 4H), 1.30 (s, 12H). ¹³C NMR (100 MHz, CD₃CN) δ 168.85, 133.67, 130.43, 111.88, 37.86, 30.84.

5 4-Nitrobenzenediazonium tetrafluoroborate (5). Yield: 67%. MP 142°C. ¹H NMR (400 MHz, CD₃CN) δ 8.72 (ABq, J = 9.4 Hz, Δv = 65.4 Hz, 4H).

10 4-Methoxycarbonylbenzenediazonium tetrafluoroborate (6). Yield 80%; MP 113°C. IR (KBr) 3103.8, 3042.4, 2955.3, 2294.7, 2310.1, 1731.4, 1582.9, 1439.5, 1306.4, 1045.23, 953.1, 860.9, 758.5, 666.3, 528.0 cm⁻¹. ¹H NMR (400 MHz CD₃CN) δ 8.51 (ABq, J=9.1 Hz, Δv=77.9 Hz, 4H), 3.97 (s, 3H). ¹³C NMR (100 MHz, CD₃CN) 165.02, 142.44, 134.12, 133.16, 119.77, 54.43.

15 4-Tetradecylbenzenediazonium tetrafluoroborate (7). The 4-tetradecylaniline was dissolved in a 1:1 mixture of acetonitrile and dry methylene chloride prior to addition to the nitrosonium tetrafluoroborate. Yield: 69%. MP 82°C. IR (KBr) 3103.8, 2919.5, 2289.6, 1577.8, 1473.7, 1070.8, 1024.8, 844.5, 813.8, 716.9, 541.0, 510.2 cm⁻¹. IR (KBr) 3103.8, 2919.5, 2289.6, 1577.8, 1473.7, 1070.8, 1024.8, 844.5, 813.8, 716.9, 541.0, 510.2 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (ABq, J = 8.8 Hz, Δv = 370.6 Hz, 4H), 2.76 (t, J = 7.7 Hz, 2H), 1.61 (quin, J = 7.8 Hz, 2H), 1.23 (s, 22H), 0.85 (t, J = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.92, 133.26, 131.94, 110.96, 37.49, 32.34, 30.87, 30.12, 30.10, 30.07, 30.04, 29.91, 29.78, 29.75, 29.72, 23.11, 14.55.

20 2-[2-(2-methoxyethoxy)ethoxy]ethyl p-toluenesulfonate (13). Sodium hydroxide (3.65 g, 91.3 mmol) and tri(ethylene glycol)monomethyl ether (10.0 g, 60.9 mmol) were dissolved in a mixture of tetrahydrofuran and water (140 mL, 20 mL, respectively). The solution was cooled in an ice bath. A solution of toluenesulfonyl chloride (12.76 g, 67.0 mmol) in 20 mL of tetrahydrofuran was added slowly. The solution was stirred at 0°C for 3 hours, then poured into 50 mL of ice water. The mixture was extracted several times with methylene chloride. The combined organic layers were washed with dilute HCl, then brine, and dried over magnesium sulfate. After filtration, the solvent was removed by distillation at reduced pressure to give 16.6 g of the product (86 % yield). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (ABq, J = 7.9 Hz, Δv = 179 Hz, 4H), 4.09 (app t, J = 4.8 Hz, 2H), 3.61 (app t, J = 4.9 Hz, 2H), 3.55 to 3.52 (m, 6H), 3.47 to 3.46 (m, 2H), 3.30 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.21, 133.28, 130.21, 128.28, 72.20, 71.00, 70.85, 69.69, 68.95, 68.26, 59.31, 21.96. IR (neat) 3503.3, 2878.5, 1597.9, 1453.1, 1356.3, 1292.0, 1247.0, 1177.2, 1097.5, 1019.0, 924.17, 818.0, 776.9, 664.5 cm⁻¹.

30 4-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]nitrobenzene (14). A portion of 13 (9.0 g, 28.3 mmol) was dissolved in 50 mL of dimethylformamide. Potassium carbonate (11.75 g, 85.0 mmol) and 4-nitrophenol (3.82 g, 27.5 mmol) were added. The solution was stirred at 80°C for 16 hours. After cooling to room temperature, the solution was poured into water and extracted three times with methylene chloride. The combined organic layers were washed with water, then brine, dried over magnesium sulfate, filtered, and the solvent was removed by distillation at reduced pressure. Chromatography (silica, hexane:ethyl acetate, 1:2) was employed to isolate the product (5.71 g, 73 % yield). IR (neat) 3109.2, 3078.2, 2878.5, 1726.3, 1588.1, 1511.2, 1337.1, 1106.7, 1050.3, 932.6,

845.5, 753.3, 656.1 cm^{-1} . ^1H NMR (CDCl_3) δ 8.07 (d, J = 9.3 Hz, 2H), 6.88 (d, J = 9.3 Hz, 2H), 4.12 (app t, 2H), 3.79 (app t, 2H), 3.62 (m, 2H), 3.58 to 3.53 (m, 4H), 3.44 to 3.42 (m, 2H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.29, 141.93, 126.24, 114.99, 72.29, 71.29, 71.03, 70.98, 69.77, 68.60, 59.44.

5 **4-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}aniline (15).** A portion of **14** (5.77 g, 20.2 mmol) was dissolved in 40 mL of acidic ethanol, and a catalytic amount of 10% palladium on carbon was added. The mixture was hydrogenated on a Parr apparatus (60 psi, 70°C) for 3 hours. The mixture was then filtered over Celite, washing with ethanol. Solid sodium bicarbonate was added, and the mixture was stirred for 2 hours and, then filtered. The solvent was removed by distillation at reduced pressure, leaving a brown oil (5.0 g, 98 % yield). IR (neat) 3441.82, 3349.64, 2893.88, 2238.41, 1634.41, 1516.36, 1449.79, 1234.71, 1101.56, 906.97, 722.62 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 6.65 (ABq, J = 8.7 Hz, $\Delta\nu$ = 51.5 Hz, 4H), 4.01 (t, J = 5.4 Hz, 2H), 3.77 (t, J = 4.6 Hz, 2H), 3.69 (app t, J = 5.6 Hz, 2H), 3.65 to 3.59 (m, 4H), 3.51 (app t, J = 4.9 Hz, 2H), 3.34 (s, 3H), 3.0 (brs, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.30, 140.58, 116.75, 116.24, 72.31, 71.14, 71.02, 70.93, 70.30, 68.49, 59.44.

15 **4-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}benzenediazonium tetrafluoroborate (9).** Compound **15** was subjected to the procedure described above for diazotization. The product was not crystalline, but rather a dark red, sticky material that was difficult to manipulate. The residue was mixed three times with ether, decanting the solvent. This material was sufficiently pure by ^1H NMR, and was used without further purification or characterization (2.17 g, 52 % yield). ^1H NMR (400, MHz, acetone- d_6) δ 8.12 (ABq, J = 9.5 Hz, $\Delta\nu$ = 479.5 Hz, 4H), 4.53 (app t, J = 4.5 Hz, 2H), 3.92 (t, J = 4.4 Hz, 2H), 3.68 to 3.66 (m, 2H), 3.61 to 3.56 (m, 4H), 3.46 (t, J = 5.4 Hz, 2H), 3.27 (s, 3H).

20 **Compound 10.** To a screw-cap tube with a magnetic stir bar was added Boc_2O (17.6 g, 80.6 mmol), 4-aminothiophenol (10.0 g, 80.6 mmol), triethylamine (13.5 mL, 96.7 mmol), 150 mL of dichloromethane, and *N,N*-dimethylaminopyridine (4.92 g, 40.3 mmol). The tube was flushed with nitrogen, and the screw-cap was installed. The solution was stirred at room temperature for 24 h. The solution was then washed with three 75 mL portions of water, the organic layer was dried over magnesium sulfate, then filtered and concentrated. The residue was chromatographed on silica using hexanes : ethyl acetate (1.5 : 1) as the eluant. The product was isolated as a clear oil that crystallized on standing (16.16 g, 94 %). mp 83-86°C. IR (KBr) 3454.5, 3376.8, 2978.6, 1711.4, 1630.1, 1597.4, 1500.0, 1384.4, 1296.0, 1201.0, 1176.3, 1125.4, 857.2, 825.2, 669.8 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ 7.32 (d, J = 8.6 Hz, 2H), 6.70 (d, J = 8.6 Hz, 2H), 3.83 (brs, 1H), 4.54 (s, 9H). ^{13}C NMR (50 MHz, CDCl_3) 169.72, 148.26, 137.05, 116.33, 115.89, 85.49, 28.63.

30 **Compound 11.** To a 500 mL round bottom flask cooled to -20 °C was added 6.74 mL of BF_3OEt_2 (171.9 mmol). To this was added a solution of **10** (3.0 g, 225.3 mmol) dissolved in 30 mL of THF, over a period of 10 min. To this was added a solution of *t*-butylnitrite (5.59 mL, 103.12 mmol) in 20 mL of THF. The solution was stirred and allowed to warm to 0 °C over 40 min, at which time 400 mL of cold ether was added. The precipitate was collected by filtration, to obtain 4.14 g (96 %)

of the desired product. ^1H NMR (400 MHz, CD_3CN) δ 8.52 (d, $J = 9.1$ Hz, 2 H), 8.0 (d, $J = 9.1$ Hz, 2 H), 1.54 (s, 9 H).

4-hydroxycarbonylphenyldiazonium tetrafluoroborate (12). This compound was prepared according to the general procedure (*vide supra*). Sulfolane was used as a co-solvent for the 4-aminobenzoic acid. Yield: 60 %. IR (KBr) 3247.9, 3105.3, 2305.5, 1732.6, 1416.1, 1386.5, 1300.1, 1232.8, 1093.1, 996.1, 906.9, 872.0, cm^{-1} . ^1H NMR (400 MHz, CD_3CN) δ 8.64 (d, $J = 9.0$ Hz, 2 H), 8.44 (d, $J = 9.0$ Hz, 2 H).

General procedure for electrochemical derivatization of SWNT-p. The apparatus used for the electrochemical derivatization experiments was a 3-electrode cell, with Ag/AgNO_3 reference electrode and platinum wire counter electrode. A piece of bucky paper (1-2 mg) served as the working electrode. The bucky paper was prepared by filtration of a 1,2-dichlorobenzene suspension over a $0.2\ \mu\text{M}$ PTFE (47 mm, Sartorius) membrane. After drying under vacuum, the paper was peeled off the membrane, and a piece was excised for use in the derivatization. The bucky paper was held with an alligator clip, previously treated with colloidal silver paste (Ted Pella, Inc.), and immersed in an acetonitrile solution of the diazonium salt (0.5 mM for **SWNT-1-SWNT-7** and **SWNT-9**; 0.01 M for **SWNT-8**) and tetra-*n*-butylammonium tetrafluoroborate (0.05 M). Care was taken not to immerse the alligator clip itself. A potential of -1.0 V was applied for a period of 30 min. Care was taken for the exclusion of light, and nitrogen was bubbled through the solution during the experiment. After reaction, the portion of the bucky paper that was not immersed in the solution was excised, and the remainder was soaked in acetonitrile for 24 hours, then washed with acetonitrile, chloroform, and ethanol. After drying, this material was sonicated in acetonitrile for 20 minutes, filtered, and washed again with acetonitrile, 2-propanol, and chloroform. The reaction products were dried under vacuum at room temperature prior to characterization. Control experiments without a diazonium salt confirm that such conditions do not affect the nanotubes, as verified by UV/vis/NIR, Raman, and TGA.

Other salts and parameters. A great variety of aryl diazonium salts for modification can be utilized in the process of the invention. Additionally, parameters such as added potential, the duration of the applied potential, the solvent, and the supporting electrolyte can be varied. Furthermore, alkyl, alkenyl and alkynyl additions could be used for the process of the invention.

B. Characterization

Scanning electron microscopy (SEM) experiments were performed on a Phillips ESEM XL-30, at an accelerating voltage of 50,000 V. This instrument was equipped with an EDAX detector. Samples for TEM imaging were drop dried from THF onto a 200 mesh lacey carbon grid on a copper support. The accelerating voltage was 100 K.V. Raman spectra were collected on a Renishaw Ramascope, on solid samples, with excitation at 782 nm. UV/Vis/NIR absorption spectra were collected on a Shimadzu UVPC-3101, in double beam mode, with solvent reference. FT-IR spectra were collected using an attenuated total reflectance (ATR) accessory. TGA data were collected in argon, on a TA Instruments SDT-2960. AFM experiments were performed in tapping mode on a Digital Multi-mode SPM. Samples for these experiments were dispersed by sonication and spin

coated on a freshly cleaved mica substrate. EMPA experiments were performed on a Cameca SX-50. The instrument was calibrated, and data were taken from several different points on each sample. The average of these points is reported below. NMR data were collected on a Bruker Avance 400. Chemical shifts are reported in ppm downfield from TMS, and referenced to solvent. Melting points are not corrected.

Electronic Structure and Optical Properties. The electronic structure and optical properties of single-wall carbon nanotubes have been well investigated. Liang, W. Z., *et al.*, *J. Am. Chem. Soc.* 2000, 122, 11129-11137; Jost, O., *et al.*, *App. Phys. Lett.* 1999, 75, 2217-2219; Wu, J., *et al.*, *App. Phys. Lett.* 2000, 77, 2554-2556. The UV/VIS/NIR absorption spectrum of **SWNT-p** and **SWNT-1** is shown in Figure 3. The features (van Hove bands) in the spectrum of **SWNT-p** are due to singularities in the density of states (DOS), and, in this spectral region, are attributed to the band gap transitions in semiconducting nanotubes. The width of these features is due to the overlap of features from tubes of different diameters and chiral indices. These transitions are no longer visible for **SWNT-1**, and the spectrum is essentially featureless. The absorption spectra of **SWNT-2** - **SWNT-7** and **SWNT-11** - **SWNT-12** are similar, with no apparent features. The spectra of **SWNT-8** (Figure 4) and **SWNT-9** retained some visible features, but these were significantly reduced relative to **SWNT-p**. The loss of structure in the absorption spectra is indicative of significant electronic perturbation of the nanotubes and disruption of the extended π network. This effect is most consistent with covalent functionalization rather than simple adsorption to nanotube walls or end caps.

Raman Spectroscopy. Raman spectroscopy of single-wall carbon nanotubes is also well developed both theoretically and experimentally. Richter, E., *et al.*, *Phys. Rev. Lett.* 1997, 79, 2738-2740; Rao, A. M., *et al.*, *Science* 1997, 275, 187-191; Li, H. D., *et al.*, *App. Phys. Lett.* 2000, 76, 2053-2055. The Raman spectrum of **SWNT-p** (Figure 5A) displays two strong bands; the radial breathing ($\omega_r \sim 230 \text{ cm}^{-1}$) and tangential ($\omega_t \sim 1590 \text{ cm}^{-1}$) modes. The multiple peaks seen in the radial breathing mode are presumably due to the distribution of tube diameters in the sample. The weaker band centered at ca. 1290 cm^{-1} (ω_d) is attributed to disorder or sp^3 -hybridized carbons in the hexagonal framework of the nanotube walls. The minor band at 850 cm^{-1} is also characteristic of these small diameter nanotubes, although its molecular origin is not certain. The spectrum of **SWNT-1** (Figure 5B) is quite different. Notably, the relative intensity of the disorder mode is much greater. This is a result of the introduction of covalently bound moieties to the nanotube framework, wherein significant amounts of the sp^2 carbons have been converted to sp^3 -hybridization. The Raman spectra of the other functionalized materials display similar modifications, relative to **SWNT-p**, but to different degrees. The frequency of the disorder mode and the relative intensities of the three major bands are shown in Table 1.

Table 1

Disorder mode frequency and intensity ratios
Of major peaks in Raman Scattering Experiments

Compound	ω_d	Int. Ratio($\omega_r : \omega_d : \omega_t$) ^{a,b}
SWNT-p	1291	1.0 : 0.3 : 2.7
SWNT-1	1295	1.0 : 2.2 : 3.3
SWNT-2	1294	1.0 : 2.2 : 4.0
SWNT-3	1295	1.0 : 2.0 : 4.0
SWNT-4	1290	1.0 : 1.4 : 3.7
SWNT-5	1291	1.0 : 1.4 : 3.7
SWNT-6	1292	1.0 : 1.5 : 3.5
SWNT-7	1293	1.0 : 1.3 : 3.8
SWNT-8	1292	1.0 : 0.7 : 3.0
SWNT-9	1293	1.0 : 0.8 : 2.5
SWNT-11	1292	1.0 : 0.8 : 2.9
SWNT-12	1291	1.0 : 1.0 : 3.4

^a ω_r = radial breathing mode, ω_d = disorder mode, ω_t = tangential mode. ^b ω_r intensity taken at 265 cm⁻¹; other intensities taken at maxima.

While there is no significant change in the frequency of the disorder mode, the intensity of this mode increased relative to the intensity of the other two modes in all cases. The intensity of the tangential mode is also increased relative to the radial breathing mode in most cases, and the overall intensity is lower. In some cases, Raman spectra collected after functionalization revealed changes in the relative intensities of the peaks within the radial breathing mode region. For example, the Raman spectra in this region is shown in Figure 6 for **SWNT-p** and **SWNT-4**.

Infrared Spectroscopy. Infrared spectroscopy (FT-IR, ATR) was also used to characterize some of the derivatized materials. The spectrum of **SWNT-4** (Figure 7A) clearly shows significant C-H stretching from the *tert*-butyl moiety at ca. 2950 cm⁻¹. In the spectrum of **SWNT-6** (Figure 7B), the carbonyl (CO) stretch is apparent at 1731 cm⁻¹ (1723 cm⁻¹ in precursor diazonium salt), along with minor C-H stretching modes in the 2900 cm⁻¹ region.

Electron Microprobe analysis. Electron microprobe analysis (EMPA) experiments revealed 2.7 atomic% chlorine for **SWNT-2** (average of four points), and 3.5 atomic% fluorine for **SWNT-3** (average of five points). These percentages correspond to estimated stoichiometries of CR_{0.036} for **SWNT-2**, and CR_{0.05} for **SWNT-3**, where C is a carbon in the nanotube framework, and R is the functionalizing moiety. Accordingly, approximately one out of every 20-30 carbons in the nanotube bears a functional moiety.

Thermogravimetric Analysis. In thermogravimetric analysis (TGA) of **SWNT-2** (Figure 8), a total weight loss of ca. 25 %, was observed on heating to 600°C under argon. After TGA of **SWNT-2**, the Raman spectrum is restored to approximately that of **SWNT-p**, as seen in Figure 9. It is

believed that this restoration indicates removal of the functional moieties, leaving the nanotubes intact. The stoichiometry estimated from the EMPA data predicts a weight loss of ca. 25% in the case of such a removal. Thus, these figures are in excellent agreement. The TGA and EMPA data for **SWNT-3** are also in good agreement. **SWNT-p** suffers a ca. 5% weight loss following the same temperature profile. TGA data and estimated stoichiometries for the remaining materials (with the exception of **SWNT-8**, which was not performed) are shown in Table 2.

Table 2

Disorder mode frequency and intensity ratios

Compound	Observed % weight loss	Stoichiometry Ratio ^a
SWNT-p	5	NA
SWNT-1	35	1/25
SWNT-2	30	1/27
SWNT-3	26	1/20
SWNT-4	27	1/34
SWNT-5	26	1/31
SWNT-6	31	1/28
SWNT-7	39	1/36
SWNT-8	--	--
SWNT-9	36	1/40
SWNT-11	28	1/44
SWNT-12	24	1/32

^a Nanotube carbons bearing a functionalized phenyl moiety. These values are compensated for weight loss at low temperatures due to solvent evaporation and degassing (ca. 2-4% in all cases).

Table 2 reflects that the degree of functionality for these compounds is at least about one moiety to forty carbon atoms, and typically at least about one moiety to thirty carbon atoms. The estimated degree of functionality is ca. out of every 20 to 30 carbons in the nanotube bearing a functionality moiety.

Scanning and Transmission Electron Microscopy. Due to insufficient resolution, analysis of the reaction products by scanning electron microscopy (SEM) did not reveal any visible evidence of functionalization or significant change from **SWNT-p**. Transmission electron microscopy (TEM) imaging of **SWNT-4** revealed significant changes due to the functionalization. In images of **SWNT-p** (Figure 10A), the nanotube walls are essentially clean and uniform, and there is no overcoating of graphitic carbon. Images of **SWNT-4** (Figure 10B) revealed the presence of bumps on the sidewalls of the tubes, on the order of 2-6 Å in dimension. These bumps are seen on almost all individual tubes and on the exterior of ropes, though the resolution is not sufficient to determine whether they are present on the walls of tubes buried within the ropes. These features are a result of functionalization.

Solubility. The solubility of single-wall carbon nanotubes is of significant interest to persons skilled in the art of the invention. The three solvents most applicable for the underivatized small-diameter nanotubes are dimethylformamide, chloroform, and 1,2-dichlorobenzene. **SWNT-4** was the only material found to offer significantly improved solubility in organic solvents. **SWNT-4** was even found to be somewhat soluble in tetrahydrofuran (THF), as opposed to a complete lack of solubility for **SWNT-p** in that solvent. After sonication for about 30 minutes, the THF solution was found to contain approximately 50 mg L⁻¹ of **SWNT-4**, with no visible particulate. After 36 hours, some visible particulate was present, but the solvent was still almost black. This dark color was retained for at least several weeks. Solubility in dimethylformamide, chloroform, and 1,2-dichlorobenzene was also improved, with suspensions being formed much more rapidly than in the case of **SWNT-p**, and higher concentrations being achievable. It is believed that this improvement in solubility is probably due to the blocking effect of the bulky *tert*-butyl group, which could inhibit the close contact necessary for "roping" of the nanotubes.

SWNT-5 and **SWNT-8** were found to be more soluble in dimethylformamide, but solubility in other solvents (tetrahydrofuran, toluene, 2-propanol, carbon disulfide) was not improved. **SWNT-9** was prepared in an effort to effect improved solubility in water and other hydrogen bonding solvents. This functionalization, however, had quite the opposite result. **SWNT-9** was not dispersible in water or water/0.2 %Triton X. Considerable difficulty was encountered in suspending **SWNT-9** in dimethylformamide.

Robustness. In an effort to assess the robustness of the functionalization and preclude simple intercalation or adsorption, **SWNT-1** was subjected to a variety of conditions. This material was sonicated for 10 minutes at both ambient temperature and 45°C, in both chloroform and 1,2-dichlorobenzene, filtered, and re-examined spectroscopically; no discernable changes were observed. Additionally, **SWNT-1** was sonicated in 1,2-dichlorobenzene for 10 minutes to disperse the tubes, then stirred at 75°C for 3 hours. After filtration and washing, no spectroscopic changes were observed.

SWNT-3 was re-examined by EMPA after additional sonication in acetonitrile, followed by filtration and washing. The fluorine content was 3.6 atomic %, as compared to 3.5 atomic % (*vide supra*), and hence within experimental limits

C. Derivatization Mechanism

While not intending to be bound by theory, it is believed that the functionalization described herein is likely initiated in a manner similar to that shown in Figure 11. The aryl radical that is presumably generated on reduction may react with a nanotube, leaving an adjacent radical that may further react or be quenched by a solvent or some impurity, or oxygen. The propensity of the initial aryl radical to dimerize or abstract a hydrogen atom from the solvent is minimized by the fact that the radical is generated at the surface of the nanotube where reaction is desired. It is noted that although the reaction may proceed through an aryl cation, the mechanism is irrelevant to the final product.

Herein lies one principle advantage of utilizing an electrochemical process, as opposed to a solution phase method in which the diazonium salt reduction is catalyzed by copper or some other metal. Since the nanotubes would be present in solution at quite low concentration, the aryl radicals would likely be quenched by some other species. Dimerization of nanotubes in the present case is also unlikely, due to lack of mobility in the solid state.

Thermal Derivatization of Carbon Nanotubes with Diazonium Species

Derivatization with aryl diazonium species is not limited to the electrochemically induced reaction. That is, both direct treatment of single-wall carbon nanotubes with aryl diazonium tetrafluoroborate salts in solution, and *in-situ* generation of the diazonium with an alkyl nitrite are effective means of functionalization. *In-situ* generation of the diazonium species has advantages in that this method can avoid the necessity of isolating and storing potentially unstable or light sensitive aryl diazonium species. The temperature utilized during the thermal reaction would be at most about 200°C, and typically at most about 60°C. In some cases, direct treatment with pre-formed diazonium salts is observed to be effective at moderate or even room temperature, and it is expected that reactions could be observed at temperatures below room temperature.

A. Examples Nos. 12-17

The nanotubes used in this investigation were again produced by a gas-phase catalytic process developed by Smalley *et al.*, and are now commercially available (Carbon Nanotechnologies Inc., HiPco material). The production material was purified by oxidation in wet air at 250°C for 24 hours, then stirring in concentrated hydrochloric acid at room temperature for 24 hours. The resulting material was washed with copious amounts of water, then 10% aqueous sodium bicarbonate, and finally with additional water. After drying under vacuum, the material was used for the functionalization reactions.

The reaction sequence is depicted in Figure 12. In a typical experiment, ~ 8 mg of single-wall carbon nanotubes was sonicated for 10 minutes in 10 mL of 1,2-dichlorobenzene (ODCB). To this suspension was added a solution of the aniline derivative (2.6 mmol, ca. 4 equiv/mol of carbon) in 5 mL of acetonitrile. After transfer to a septum capped reaction tube (Ace Glass, #8648-03) and bubbling with nitrogen for 10 min, 4.0 mmol of isoamyl nitrite was quickly added. The septum was removed and replaced with a Teflon screw-cap, and the suspension was stirred at 60°C for approximately 15 hours. Due to the system utilized, considerable pressure was attained in the vessel due to the evolved nitrogen. This was alleviated by partially unscrewing the cap for venting every ~30 min for the first 3 hours.

After cooling to ~ 45°C, the suspension was diluted with 30 mL of dimethylformamide (DMF), filtered over a Teflon (0.45 µm) membrane, and washed extensively with DMF. Repeated sonication in, and further washing with DMF constituted purification of the material.

B. Characterization

Functionalized nanotube materials **16–19** and **21** displayed significantly altered spectroscopic properties, akin to those reported for materials derivatized via the electrochemical method described above. For example, the UV/vis/NIR absorption spectrum of **18** (Figure 13) shows an almost

complete loss of the van Hove singularities. This loss of structure is characteristic of the disrupted π -system, and again indicates covalent modification of the nanotubes. In the Raman spectra reflected in Figure 14, the overall intensity of the scattered light is lower, and the relative intensities of the three main modes are altered.

5 Relative to the tangential mode at ca. 1590 cm^{-1} , the intensity of the radial breathing mode (ca. 250 cm^{-1}) is decreased, and the intensity of the disorder mode (1290 cm^{-1}) is significantly increased. The increase in the relative intensity of the disorder mode can be attributed to an increased number of sp^3 -hybridized carbons in the nanotube framework, and can be taken as a crude measure of the degree of functionalization. Additionally, as previously discussed, the
10 functionalized phenyl moieties attached to the nanotubes can be removed by heating in an argon atmosphere, and that thermal gravimetric analysis (TGA) consequently provides a quantitative estimate of the degree of functionalization. Upon heating **16** – **19** to 600°C in an argon atmosphere, the observed weight loss values were as follows, with the value previously reported for the same materials prepared via the electrochemical technique in parenthesis: **16**: 26% (30%), **17**: 25%
15 (27%), **18**: 26% (31%), **19**: 23% (26%) **21** (not prepared by the electrochemical technique). Material **20** did not display similar changes in the spectroscopic properties or significant mass loss in TGA, even though this moiety can be successfully attached by the electrochemical technique. The ester bearing material **18** was successfully prepared, in principle giving access to the carboxylic acid moiety via hydrolysis.

20 It is of primary interest to compare the degree of functionalization achievable by the thermal process to that obtained by the electrochemical processes of the present invention. Experiment Nos. 13-18 were performed with a large excess of the aniline derivative, *i.e.* sufficient to provide the diazonium species in amounts equivalent to the amount of diazonium tetrafluoroborate salts used in the previously discussed reported electrochemical examples. Hence, these Examples Nos. 13-18
25 are comparable in this fashion.

 For material **16**, straightforward comparison is available through electron microprobe analysis. This analysis gave a value of 2.2 atomic % chlorine, relative to 97 atomic % carbon. Similar material prepared by the electrochemical technique was analyzed to have 2.7 atomic % chlorine, relative to 96 atomic % carbon (*vide supra*).

30 The TGA data also give additional insight into the relative efficiency of the thermal method. For example, the mass loss for **19** corresponds to an estimated 1 in 37 carbons in the nanotubes being functionalized, versus the 1 in 34 ratio achieved by the electrochemical method. It is believed that the thermal technique is then comparable in its effectiveness to the electrochemical method for the equivalent material (**SWNT-5**). It is believed that optimization of the conditions could provide a
35 higher degree of functionalization. The observed efficacy is sufficient to significantly alter the properties of the single-wall carbon nanotubes, and will likely be satisfactory for numerous applications, such as cross-linked materials and composite formation as discussed below.

The thermal reaction of the present invention was found to be nearly as efficacious as the electrochemical process of the present invention, although, in certain respects, this thermal reaction is simpler to execute and more adaptable for scalability.

It is again noted that the chemical derivatization of nanotubes can also be successfully performed using pre-formed diazonium species. The diazonium species can be prepared beforehand, isolated, and added to the mixture. The derivatization can then be induced thermally. Additional variations include variations in the temperature of the process (ambient temperature and higher and lower temperatures), ratio of reactants, and a variety of organic solvents.

Photochemical Derivatization of Carbon Nanotubes with Diazonium Species

Example No. 18. Derivatization with aryl diazonium species can also be induced photochemically. A photochemical reaction was performed utilizing 4-chlorobenzenediazonium tetrafluoroborate, which is the same diazonium species prepared and utilized in Example No. 2. Thus, a suspension of **SWNT-p** in 1,2-dichlorobenzene was created by sonication. To this suspension was added a portion of the diazonium salt dissolved in minimal acetonitrile. The resulting mixture was stirred while residing within the chamber of a photochemical reaction apparatus, with an excitation wavelength of ca. 254 nm (an ultraviolet light source). The light source for the photochemically induced reaction may be any wavelength, and typically is an ultraviolet or visible wavelength. This reaction is reflected in Figure 15. The resultant material was similar in all respects to **SWNT-2** that was prepared by the electrochemical technique of the present invention.

This experiment further confirmed that reaction of the diazonium salt leads to covalent attachment to the nanotube.

Controlled, Site-Specific Functionalization of Carbon Nanotubes with Diazonium Species

By utilizing the electrochemically induced reaction of the present invention, control can be exerted to derivatize the nanotubes at specific sites. Existing technologies (M.S. Fuhrer, *et.al.*, "Crossed Nanotube Junctions" *Science*, 288, 21 April 2000, page 494; Yu Huang, *et.al.*, "Directed Assembly of One-Dimensional Nanostructures into Functional Networks" *Science*, 291, 26 January 2001, page 630; Yi Cui, *et al.* "Functional Nanoscale Electronics Devices Assembled Using Silicon Nanowire Building Blocks" *Science*, 291, 2 February 2001, p 851) can be used to prepare a crossbar architecture of nanotubes, wherein one nanotube is fixed to a substrate and a second nanotube is suspended a finite distance above. Both nanotubes can be individually addressed electrically. Application of opposite potentials to the two tubes causes the top tube to deform and essentially come into contact with the lower tube. "Contact" as used herein means both actual physical contact, but also proximity of the entities within an infinitesimally small distance (referred to as van der Waals contact), in which the entities may influence each other on a molecular and electronic scale.

This deformation results in two features of significance. First, the top tube is physically deformed, leading to a potentially higher chemical reactivity at the point of deformation, based on current understanding of the effects of curvature strain on reactivity. This feature would allow

selective functionalization at the junction via the electrochemical technique of reaction with diazonium salts. Secondly, higher potential is achieved at the point of "cross" between the tubes.

In the present invention, directed functionalization of the crossed-nanotube junctions can be performed by applying a potential to the ends of the nanotubes (as is known in the art) in the presence of α,ω -bis(diazonium) salts or mono-diazonium salts with an interacting group at the opposite end would permit functionalization at the cross point domain.

Any cross bar array of nanotubes could be functionalized by such processes. For instance, a crossbar architecture of nanotubes will be prepared by fluid flow over a patterned substrate, or by direct tube growth between posts, or by some other method. Furthermore, the diazonium salt assembly described here could occur in a diazonium solution, with voltages on orthogonal tubes, regardless of the assembly method for the tube arrays. Application of potentials to the nanotubes in the presence of diazonium salts would permit functionalization at the cross point domain.

The diazonium species are directed by the potential existing at the junction to react with the surface of the nanotube, thus placing functional molecular devices at the junctions. Site-specific functionalization could enable the use of nanotubes in molecular electronic applications since device functionality is critical at the cross points. The crossed nanotubes therefore provide a method of directly addressing the functionalized molecules, including molecules that function as molecular switches, molecular wires, and in other capacities and uses as is generally known in the art.

Furthermore, this process would allow for attachment of different molecules to nanotube cross points, *i.e.*, controlled attachment of two or more different chemical functionalities to different locations on nanotubes. This would be performed by applying a potential at a specified set of positions while in a solution of a first diazonium salt, then moving to a solution of a second diazonium salt and applying a potential at other positions, *etc.* In addition, site specific functionalization will allow individual molecules or groups of molecules to be electrically addressed by metallic contact pads or other contact means as are known in the art. Just such a molecule of electronic interest is incorporated into SWNT-8.

Application of chemically modified carbon nanotubes in polymer composite materials

Polymer and polymer/composite materials are widely used for structural materials and a variety of other applications. The derivatized carbon nanotubes made using the processes disclosed herein can be used in combination with existing polymer matrices to create new polymer/composite materials. In general, possible composite materials could be made with chemically modified nanotubes and thermoplastics, thermosets, elastomers, and others. There are a multitude of variations in the chemical structure of the polymer matrix, *i.e.* polyethylene, various epoxy resins, polypropylene, polycarbonate *etc.* There is also a host of variations possible in the chemical groups that can be attached to the nanotubes. According, it is possible to select a specific polymer and specific moiety to enhance the properties of the particular polymer/composite material desired.

Thus, the polymer/composite material will have significantly enhanced properties, such as, for example, enhanced strength and/or conductivity. And, when modified with suitable chemical groups,

the nanotubes will be chemically compatible with the polymer matrix, allowing transfer of the properties of the nanotubes (especially mechanical strength) to the properties of the composite material as a whole. Typically, to achieve this, the modified carbon nanotubes can be thoroughly mixed (physically blended) with the polymeric material, and allowed to react at ambient or elevated temperature.

Thermosets. It may be desired to form a polymer/composite material in which the carbon nanotubes are chemically bound at multiple points to the polymer (thermosets). For example, this can be done, for example, utilizing an epoxy resin. Epoxy resins are typically composed of two portions that are mixed in a certain ratio. The resulting mixture then hardens, or "cures," over a period of time into an adhesive or structural material. The two parts are the epoxy portion (labeled "A" in Figure 16, in this case derived from the reaction of bisphenol-A with epichlorohydrin) and the curing agent (labeled "B" in Figure 16). The curing agent contains chemical groups that react with a repeatedly occurring chemical group in the epoxy portion. *I.e.*, the cured or cross-linked resin results from the reaction of A (specifically, the terminal epoxide functionalities) with B (specifically, the terminal amine functionalities). Because both the epoxy portion and the curing agent contain numerous reactive groups, a "cross-linked" material is created, with numerous chemical bonds that impart strength to the cured material (labeled "C" in Figure 16). The result of the reaction is a highly cross-linked thermoset material.

A wide variety of commercially available epoxy components exist, where the chemical structure of both parts A and B can vary greatly. For example, curing agents may be based on diamines, polymercaptans, phenol containing materials, *etc.*, and may be polymeric. The addition of chemically modified carbon nanotubes to this type of system will greatly increase the strength of the resulting material, due to the strength of the nanotubes themselves. The nanotubes can be chemically modified with groups that are compatible with either the epoxy portion or the curing agent portion. For example, modified nanotubes can be prepared as shown in Figure 17. (In the figures, the shaded cylinder represents the carbon nanotubes).

Carbon nanotubes thus modified will be thoroughly mixed with either the curing agent portion or the epoxy portion. The resulting material will then be thoroughly mixed with the second portion and allowed to react, or cure at either ambient or elevated temperature, depending on the particular system. The resulting composite material will then be cross-linked not only by the curing agent, but also by the modified carbon nanotubes, *via*, for example, aryl-thioether linkages, as shown in Figure 18, where the freehand lines schematically represent the polymer matrix.

These types of materials can be prepared using a variety of modified carbon nanotubes, exemplified by the examples in Figure 17. Thus, the linkages between the polymer matrix and the nanotubes could be ether, thioether, amine, salt bridge (such as **SWNT-11** in an amine containing host polymer) or other linkages. It is understood that the direct chemical bond between the nanotubes and the surrounding polymer matrix will enable the transference of the strength properties of the nanotubes to the composite material itself. It is also noted that enhancement of the material properties by the nanotubes may be caused by factors other than such direct chemical

bonding; for example, improved dispersion of the nanotubes within the polymer matrix, enabled by the functionalization, may allow enhancement.

In addition to the chemical bond between the nanotubes and the surrounding polymer matrix, in the case of thiophenol derivatized nanotubes, there will be a chemical interaction between the nanotubes themselves. The formation of disulfide linkages between nanotubes, as shown in Figure 19, will serve to further strengthen the material. The disulfide linkages can be further reduced (chemically, for instance) to once again provide the non-crosslinked tubes. Hence, this is a stealth-like crosslinking. In fact, such cross-linked nanotubes will represent an enhanced strength material in their own right for some applications.

Another possibility is modification of carbon nanotubes with chemical groups that are compatible with the epoxy portion rather than the curing agent portion, such as, for example, shown in Figure 21. The material resulting from the incorporation of nanotubes derivatized in this manner would again be a chemically bound, three-dimensional network, cross-linked by both the curing agent and the chemically modified nanotubes.

Other specific chemical interactions between modified carbon nanotubes and a polymer matrix are also possible. For example, a system based on a hydrogen bonding interaction is shown in Figure 22. This type of interaction would be in an extended three-dimensional network, again imparting the strength of the nanotubes to the composite material.

Utilizing the electrochemical process described in this invention, the derivatized nanotubes reflected in Figure 20 were prepared. From this, what is believed to be a step of deprotection of the thiol was performed by treatment with trifluoroacetic acid in 1,2-dichlorobenzene (acid hydrolysis). Alternatively, this step could be performed by treatment with trifluoroacetic acid in dimethylformamide, or by thermolysis at or about 175°C. Again, the functionalized nanotubes formed as reflected in Figure 20 would chemically react with, for example an epoxy resin, with the free thiol group (SH) acting as a crosslinking agent.

Thermoplastics. In addition to thermosets, derivatized nanotubes can be utilized for thermoplastics. As in the case of thermosets, the derivatized nanotubes may or may not be chemically bound to the polymer matrix. It is understood that a modest degree of chemical attachment between the derivatized nanotubes and the polymer matrix could be tolerated, while retaining the thermoplastic properties (specifically, the ability to heat and reform the material without significant degradation). As noted above, physical blending of the carbon nanotubes with the polymer can be enhanced by the derivatization process (specifically by making the nanotubes more compatible with, or more soluble in, the host polymer).

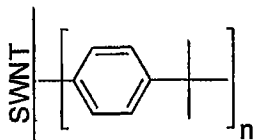
For instance, a polymer/composite material containing pure (and underivatized) single-wall carbon nanotubes may be desired so that the polymer would have certain enhanced conductive properties; however, the pure and underivatized carbon nanotubes may not sufficiently disperse in the polymer. By derivatizing the nanotubes with a particular moiety, the derivatized nanotubes could then be dispersed adequately. Because the derivatization of the nanotube may likely have affected the conductivity of the nanotube (and will thus effect the conductivity of the polymer/composite), it

may be desirable to reverse the derivatization process to remove the functional groups from the nanotubes after dispersal. In this manner, the conductivity of the material can be recovered. This can be done by any process that reverses the derivatization, such as raising the temperature of the polymer/composite material to a temperature at which the functional group disassociates. Typically, this temperature appears to be at least about 250°C.

A. Example Nos. 19-25

Moreover, the thermoplastic may also be formed utilizing the derivatized carbon nanotube. The functional groups, while not necessarily chemically bond to the polymer, would be physical extensions from the tube (like branches from a tree) that will afford additional strength to the polymer/composite materials. This enhancement may be due to a roughening effect on the nanotube surface, increasing friction and reducing sliding of the polymer matrix along the nanotube length. As is understood in the art, such an effect would further enable transference of the desirable nanotube properties to the composite material.

Utilizing processes discussed above the following functionalized single-wall carbon nanotubes where prepared where $n = 1$ in 20 to 1 in 40 functional groups per nanotube carbons):



17

This derivatized material (17) was dispersed in High-Impact-Polystyrene (HIPS) at various concentrations. Tensile strength, tensile modulus, and % strain to failure data of the resulting composite material were then gathered. The results of these examples are reflected in Table 3.

Table 3

Material	Tensile Strength (MPa)	Tensile Modulus (MPa)	% Strain to Failure
HIPS (pure)	18.1	454.5	56.4
1 wt % 17	32.5	729.3	4.6
3 wt % 17	17.8	821.3	2.2
3 wt % pristine*	22.8	560.0	11.0
5 wt % 17	26.3	736.5	3.9
7 wt % 17	22.0	724.4	3.1

*3 wt. %, unfunctionalized nanotubes (SWNT-p), for direct comparison

On the whole, there is a substantial improvement in the tensile properties of the polymer/composite materials with the functionalized nanotubes. There is improvement over both the pristine HIPS polymer, and over the composite of HIPS and unfunctionalized nanotubes.

Polymerization. Furthermore, a polymer that includes carbon nanotubes can be formed by derivatizing the carbon nanotubes with a functional group that is capable of polymerizing or initiating a polymerization. Once the functional group is attached, standard polymerization techniques can

then be employed to grow the polymer from the functional group *in situ*. I.e., the functional group attached to the nanotube could be used as a generator of polymer growth. Such standard polymerization techniques could be any of the standard known types, such as radical, cationic, anionic, condensation, ring-opening, methathesis, or ring-opening-metathesis (ROMP) polymerizations, when appropriate groups are bound to the nanotubes. For instance, Figure 23 reflects an example of a carbon nanotube that has been derivatized with a functional group 4-aminophenyl that is subsequently polymerized with styrene to grow the polymer from the functional group. Accordingly, the functional group attached to the nanotube would be a chemically active part of the polymerization, which would result in a composite material in which the nanotubes are chemically involved.

All of the compositions and methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. More specifically, it will be apparent that certain agents which are both chemically and physiologically related may be substituted for the agents described herein while the same or similar results would be achieved. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the invention as defined by the appended claims.

CLAIMES:

1. A method for derivatizing sidewalls of carbon nanotubes comprising:
 - (a) selecting a plurality of carbon nanotubes; and
 - (b) reacting the plurality of carbon nanotubes with a diazonium specie.
- 5 2. A method comprising:
 - (a) selecting a plurality of carbon nanotubes;
 - (b) reacting the plurality of carbon nanotubes with a diazonium specie to form derivatized carbon nanotubes;
 - (c) dispersing the derivatized carbon nanotubes in a solvent.
- 10 3. A method for derivatizing single-wall carbon nanotubes comprising:
 - (a) selecting an assembly of single-wall carbon nanotubes;
 - (b) immersing the assembly in a solution comprising a diazonium specie; and
 - (c) applying a potential to the assembly to electrochemically react the assembly with the diazonium specie.
- 15 4. A method for derivatizing single-wall carbon nanotubes comprising:
 - (a) selecting a plurality of single-wall carbon nanotubes;
 - (b) preforming a diazonium specie; and
 - (c) reacting the plurality of single-wall carbon nanotubes with the preformed diazonium specie.
- 20 5. A method for derivatizing single-wall carbon nanotubes comprising:
 - (a) selecting a plurality of single-wall carbon nanotubes;
 - (b) mixing a precursor of a diazonium specie with the plurality of single-wall carbon nanotubes;
 - (c) generating the diazonium specie; and
 - 25 (d) reacting the plurality of single-wall carbon nanotubes with the diazonium specie.
6. The method of claims 1 or 2, wherein the plurality of carbon nanotubes comprise single-wall carbon nanotubes.
7. The method of claims 3, 4, 5, or 6, wherein the single-wall carbon nanotubes have an average diameter of at most about 0.7 nm.
- 30 8. The method of claims 1, 2, or 4, wherein the plurality are electrochemically reacted with the diazonium specie.
9. The method of claims 1 or 2, wherein the plurality are thermally reacted with the diazonium specie.
10. The method of claims 5 or 9, wherein the diazonium specie is generated *in situ*.
- 35 11. The method of claims 1 or 2, wherein the diazonium specie is preformed before the plurality are thermally reacted with the diazonium specie.
12. The method of claims 1, 2, or 4, wherein the plurality are photochemically reacted with the diazonium specie.

13. The method of claims 1, 2, 3, 4, or 5, wherein the diazonium specie comprises an aryl diazonium specie.

14. The method of claims 1, 2, 3, 4, or 5, wherein the diazonium specie comprises a species selected from the group consisting of an alkyl diazonium specie, an alkenyl diazonium specie, an alkyny diazonium specie, and combinations thereof.

15. The method of claims 1, 2, 4, or 5, wherein the plurality is an assembly of carbon nanotubes.

16. The method of claim 1, 2, 3, 4, or 5 wherein the assembly is selected from the group consisting of a bucky paper and a mat.

17. The method of claims 1, 2, or 4 further comprising:

- (a) immersing the assembly in a solution comprising the diazonium specie; and
- (b) applying a potential to the assembly.

18. The method of claims 3 or 17, wherein the potential is a negative potential.

19. The method of claims 3 or 17, wherein the solution further comprises a supporting electrolyte specie.

20. The method of claims 1, 2, 3, 4, 17, or 18, wherein the step of applying a potential to the assembly comprises holding the assembly with an alligator clip treated with a colloidal silver paste.

21. The method of claims 1, 2, 3, 4, or 5, wherein the diazonium specie comprises a diazonium salt.

22. The method of claim 21, wherein the diazonium salt comprises a salt selected from the group consisting of an aryl diazonium salt, an alkyl diazonium salt, an alkenyl diazonium salt, an alkyny diazonium salt, and combinations thereof.

23. The method of claims 1, 2, 3, 4, or 5 further comprising sonicating the derivatized carbon nanotubes.

24. The method of claims 1, 2, 3, 4, or 5, wherein the amount of a moiety bonded to the carbon atoms of a carbon nanotube is at a moiety to carbon ratio at least about one moiety to forty carbon atoms.

25. The method of claims 1, 2, 3, 4, or 5, wherein the amount of a moiety bonded to the carbon atoms of a carbon nanotube is at a moiety to carbon ratio at least about one moiety to thirty carbon atoms.

26. The method of claims 1, 2, 4, or 5, wherein the reaction is a thermal reaction at a temperature of at most about 200°C.

27. The method of claims 1, 2, 4, or 5, wherein the reaction is a thermal reaction at a temperature of at most about 60°C.

28. The method of claims 1, 2, 3, 4, or 5 further comprising removing functional moieties from the derivatized carbon nanotubes.

29. The method of claim 28, wherein the removal step comprises heating the derivatized carbon nanotubes.

30. The method of claim 29, wherein the derivatized carbon nanotubes are heated to a temperature at least about 250°C.

31. The method of claim 29, wherein the derivatized carbon nanotubes are heated to a temperature at least about 600°C.

32. The method of claims 1, 2, or 4 further comprising photochemically reacting the plurality of single-wall carbon nanotubes and the diazonium specie.

33. The method of claim 32, wherein the photochemical reaction comprises the use of an ultraviolet light source.

34. The method of claim 32, wherein the photochemical reaction comprises the use of a visible light source.

35. The method of claim 5, wherein the precursor of diazonium specie is an aniline derivative precursor of the diazonium specie and the diazonium specie is generated with a nitrite.

36. A product made by the process comprising:

- (a) selecting a plurality of carbon nanotubes; and
- (b) reacting the plurality of carbon nanotubes with a diazonium specie.

37. A product made by the process comprising:

- (a) selecting a plurality of carbon nanotubes;
- (b) reacting the plurality of carbon nanotubes with a diazonium specie to form derivatized carbon nanotubes;
- (c) dispersing the derivatized carbon nanotubes in a solvent.

38. A product made by the process comprising:

- (a) selecting an assembly of single-wall carbon nanotubes;
- (b) immersing the assembly in a solution comprising a diazonium specie; and
- (c) applying a potential to the assembly to electrochemically react the assembly with the diazonium specie.

39. A product made by the process comprising:

- (a) selecting a plurality of single-wall carbon nanotubes;
- (b) preforming a diazonium specie; and
- (c) reacting the plurality of single-wall carbon nanotubes with the preformed diazonium specie.

40. A product made by the process comprising:

- (a) selecting a plurality of single-wall carbon nanotubes;
- (b) mixing a precursor of a diazonium specie with the plurality of single-wall carbon nanotubes;
- (c) generating the diazonium specie; and
- (d) reacting the plurality of single-wall carbon nanotubes with the diazonium specie.

41. The product of claims 36 or 37, wherein the plurality of carbon nanotubes comprise single-wall carbon nanotubes.

42. The product of claims 38, 39, 40, or 41, wherein the single-wall carbon nanotubes have an average diameter of at most about 0.7 nm.

43. The product of claims 36, 37, or 39 wherein the plurality are electrochemically reacted with the diazonium specie.

44. The product of claims 36 or 37, wherein the plurality are thermally reacted with the diazonium specie.

5 45. The product of claims 40 or 44, wherein the diazonium specie is generated *in situ*.

46. The product of claims 36 or 37, wherein the diazonium specie is preformed before the plurality are thermally reacted with the diazonium specie.

47. The product of claims 36, 37, or 39 wherein the plurality are photochemically reacted with the diazonium specie.

10 48. The product of claims 36, 37, 38, 39, or 40, wherein the diazonium specie comprises an aryl diazonium specie.

49. The product of claims 36, 37, 38, 39, or 40, wherein the diazonium specie comprises a species selected from the group consisting of an alkyl diazonium specie, an alkenyl diazonium specie, an alkynyl diazonium specie, and combinations thereof.

15 50. The product of claims 36, 37, 39, or 40, wherein the plurality is an assembly of carbon nanotubes.

51. The product of claim 36, 37, 38, 39, or 40, wherein the assembly is selected from the group consisting of a bucky paper and a mat.

52. The product of claims 36, 37, or 39 further made by the process comprising:

20 (a) immersing the assembly in a solution comprising the diazonium specie; and

(b) applying a potential to the assembly.

53. The product of claims 38 or 52, wherein the potential is a negative potential.

54. The method of claims 38 or 52, wherein the solution further comprises a supporting electrolyte specie.

25 55. The product of claims 36, 37, 38, 39, 52 or 53, wherein the step of applying a potential to the assembly comprises holding the assembly with an alligator clip treated with a colloidal silver paste.

56. The product of claims 36, 37, 38, 39, or 40, wherein the diazonium specie comprises an a diazonium salt.

30 57. The product of claim 56, wherein the diazonium salt comprises a salt selected from the group consisting of an aryl diazonium salt, an alkyl diazonium salt, an alkenyl diazonium salt, an alkynyl diazonium salt, and combinations thereof.

58. The product of claims 36, 37, 38, 39, or 40, further made by the process comprising sonicating the derivatized carbon nanotubes.

35 59. The product of claims 36, 37, 38, 39, or 40, wherein the amount of a moiety bonded to the carbon atoms of a carbon nanotube is at a moiety to carbon ratio at least about one moiety to forty carbon atoms.

60. The product of claims 36, 37, 38, 39, or 40, wherein the amount of a moiety bonded to the carbon atoms of a carbon nanotube is at a moiety to carbon ratio at least about one moiety to thirty carbon atoms.

61. The product of claims 36, 37, 39, or 40, wherein the reaction is a thermal reaction at a temperature of at most about 200°C.

62. The method of claims 36, 37, 39, or 40, wherein the reaction is a thermal reaction at a temperature of at most about 60°C.

5 63. The product of claims 36, 37, 38, 39, or 40 further comprising removing functional moieties from the derivatized carbon nanotubes.

64. The product of claims 36, 37, or 39 further comprising photochemically treating the mixture of the plurality of single-wall carbon nanotubes and the diazonium specie.

10 65. The product of claim 64, wherein the photochemical treatment comprises the use of an ultraviolet light source.

66. The product of claim 64, wherein the photochemical treatment comprises the use of a visible light source.

67. The product of claim 40, wherein the precursor of the diazonium specie is an aniline derivative precursor of the diazonium specie and the diazonium specie is generated with a nitrite.

15 68. A solution of single-wall carbon nanotubes made by the process of:

(a) a plurality of derivatized single-wall carbon nanotubes, wherein the plurality of derivatized carbon nanotubes were derivatized utilizing a diazonium specie;

(b) a solvent, wherein the derivatized plurality of carbon nanotubes are dispersed in the solvent.

20 69. A process comprising:

(a) derivatizing a carbon nanotube with a diazonium specie; and

(b) covalently attaching a molecular wire to the derivatized carbon nanotube.

70. A process comprising:

(a) derivatizing a carbon nanotube with a diazonium specie; and

25 (b) covalently attaching a molecular switch to the derivatized carbon nanotube.

71. The process of claims 69 or 70, wherein the carbon nanotube is a single-wall carbon nanotube.

72. The process of claims 69 or 71 further comprising connecting a molecular electronic device to the molecular wire.

30 73. The process of claims 69, 71, or 72, wherein the molecular wire comprises an oligo(phenylene ethynylene) molecular wire.

74. A product comprising:

(a) derivatized carbon nanotube; and

(b) a molecular wire covalently attaching to the derivatized carbon nanotube.

35 75. A product comprising:

(a) derivatized carbon nanotube; and

(b) a molecular switch covalently attaching to the derivatized carbon nanotube.

76. The product of claims 74 or 75, wherein the carbon nanotube is a single-wall carbon nanotube.

77. The product of claims 74 or 76 further comprising a molecular electronic device connected to the molecular wire.

78. The product of claims 74, 76, or 77, wherein the molecular wire comprises an oligo(phenylene ethynylene) molecular wire.

5 79. A method for derivatizing carbon nanotubes comprising:

(a) preparing an assembly, wherein

(i) the assembly comprises a first plurality of carbon nanotubes and a second plurality of carbon nanotubes; and

10 (ii) wherein the carbon nanotubes in the first plurality and the carbon nanotubes in the second plurality can be individually addressed electronically;

(b) immersing the assembly in a diazonium specie; and

(c) applying a negative potential to the assembly to cause the first plurality to essentially come in contact with the second plurality; and

(d) electrochemically reacting the assembly with the diazonium specie.

15 80. A method for derivatizing carbon nanotubes comprising:

(a) preparing an assembly of carbon nanotubes

(b) immersing the assembly in a first diazonium specie;

(c) applying a potential to the assembly in a first direction;

(d) electrochemically reacting the assembly with the first diazonium specie;

20 (e) immersing the assembly in a second diazonium specie;

(f) applying a potential to the assembly in a second direction; and

(g) electrochemically reacting the assembly with the second diazonium specie.

81. The method of claims 79 or 80, wherein the carbon nanotubes of the first plurality comprise single-wall carbon nanotubes and the carbon nanotubes of the second plurality comprise single-wall carbon nanotubes.

82. The method of claims 79, 80, or 81, wherein the assembly is a crossbar architecture of carbon nanotubes.

83. The method of claims 79, 80, 81, or 82, wherein the preparation of the assembly comprises fluid flow over a patterned surface.

30 84. The method of claims 79, 80, 81, or 82, wherein the preparation of the assembly comprises direct carbon nanotube growth between posts.

85. The method of claims 79, 80, 81, or 82, further comprising connecting functionalized molecules to the assembly.

86. The method of claim 85, wherein the functionalized molecules comprise molecules that function in a capacity selected from the group consisting of molecular switches and molecular wires.

87. The method of claims 79, 80, 81, or 82, further comprising operatively connecting molecular electronic devices to the assembly.

88. A product made by the process comprising:

(a) preparing an assembly, wherein

(i) the assembly comprises a first plurality of carbon nanotubes and a second plurality of carbon nanotubes; and

(ii) wherein the carbon nanotubes in the first plurality and the carbon nanotubes in the second plurality can be individually addressed electronically;

5 (b) immersing the assembly in a diazonium specie; and

(c) applying a negative potential to the assembly to cause the first plurality to essentially come in contact with the second plurality; and

(d) electrochemically reacting the assembly with the diazonium specie.

89. A product made by the process comprising:

10 (a) preparing an assembly of carbon nanotubes

(b) immersing the assembly in a first diazonium specie;

(c) applying a potential to the assembly in a first direction;

(d) electrochemically reacting the assembly with the first diazonium specie;

(e) immersing the assembly in a second diazonium specie;

15 (f) applying a potential to the assembly in a second direction; and

(g) electrochemically reacting the assembly with the second diazonium specie.

90. The product of claims 88 or 89, wherein the carbon nanotubes of the first plurality comprise single-wall carbon nanotubes and the carbon nanotubes of the second plurality comprise single-wall carbon nanotubes.

20 91. The product of claims 88, 89, or 90, wherein the assembly is a crossbar architecture of carbon nanotubes.

92. The product of claims 88, 89, 90, or 91, wherein the preparation of the assembly comprises fluid flow over a patterned surface.

25 93. The product of claims 88, 89, 90, or 91, wherein the preparation of the assembly comprises direct carbon nanotube growth between posts.

94. The product of claims 88, 89, 90, or 91, wherein the process further comprises connecting functionalized molecules to the assembly.

95. The product of claim 94, wherein the functionalized molecules comprise molecules that function in a capacity selected from the group consisting of molecular switches and molecular wires.

30 96. The product of claims 88, 89, 90, or 91, wherein the process further comprises operatively connecting molecular electronic devices to the assembly.

97. A method for making a polymer material comprising:

35 (a) derivatizing carbon nanotubes with functional moieties to form derivatized carbon nanotubes, wherein the functional moieties are derivatized to the carbon nanotubes utilizing a diazonium specie;

(b) dispersing the derivatized carbon nanotubes in a polymer.

98. The method of claim 97, wherein the carbon nanotubes are single-wall carbon nanotubes.

99. The method of claims 97 or 98, wherein the functional moieties are chemically bound to the polymer.

100. The method of claims 97 or 98, wherein the functional moieties are not chemically bound to the polymer.

101. The method of claims 97 or 98, wherein the functional moieties are removed after the dispersing step.

102. The method of claim 101, wherein the removal step comprises heating the dispersal of the derivatized carbon nanotubes and the polymer to a temperature at least about 250°C.

103. The method of claim 101, wherein the removal step comprises heating the dispersal of the derivatized carbon nanotubes and the polymer to a temperature at least about 600°C.

104. The method of claims 97 or 98, wherein the functional moiety is operable to react with a curing agent.

105. The method of claims 104, wherein the polymer comprises the curing agent.

106. The method of claim 104, wherein the curing agent is dispersed in the dispersal of the derivatized carbon nanotubes and the polymer.

107. The method of claims 104, 105, or 106, wherein the curing agent comprises an agent selected from the group consisting of diamines, polymercaptans, and phenol containing materials.

108. The method of claims 97 or 98, wherein the functional moiety is operable to react with an epoxy portion.

109. The method of claims 108, wherein the polymer comprises the epoxy portion.

110. The method of claims 104, 105, 106, 107, 108, or 109 further comprising curing the dispersal of the derivatized carbon nanotubes and the polymer.

111. A polymer material comprising:

(a) derivatized carbon nanotubes, wherein the derivatized carbon nanotubes comprise a diazonium species moiety; and

(b) a polymer, wherein the derivatized carbon nanotubes are dispersed in the polymer.

112. A polymer material comprising:

(a) derivatized carbon nanotubes, wherein the derivatized carbon nanotubes were derivatized utilizing a diazonium species; and

(b) a polymer, wherein the derivatized carbon nanotubes are dispersed in the polymer.

113. A polymer material made by the process comprising:

(a) derivatizing carbon nanotubes with functional moieties to form derivatized carbon nanotubes, wherein the functional moieties are derivatized to the carbon nanotubes utilizing a diazonium specie;

(b) dispersing the derivatized carbon nanotubes in a polymer.

114. The polymer material of claims 111, 112, or 113, wherein the carbon nanotubes are single-wall carbon nanotubes.

115. The polymer material of claims 111, 112, 113, or 114, wherein the functional moieties are chemically bound to the polymer.

116. The polymer material of claims 111, 112, 113, or 114, wherein the functional moieties are not chemically bound to the polymer.

117. The polymer material of claims 111, 112, 113, or 114, wherein the functional moiety is operable to react with a curing agent.

118. The polymer material of claims 117, wherein the polymer comprises the curing agent.

119. The polymer material of claim 117, wherein the curing agent is dispersed in the dispersal of the derivatized carbon nanotubes and the polymer.

120. The polymer material of claims 117, 118, or 119, wherein the curing agent comprises an agent selected from the group consisting of diamines, polymercaptans, and phenol containing materials.

121. The polymer material of claims 111, 112, 113, or 114, wherein the functional moiety is operable to react with an epoxy portion.

122. The polymer material of claims 121, wherein the polymer comprises the epoxy portion.

123. The polymer material of claims 117, 118, 119, 120, 121, or 122, wherein the process further comprises curing the dispersal of the derivatized carbon nanotubes and the polymer.

124. A method for making a polymer material comprising:

(a) derivatizing carbon nanotubes with functional groups to form derivatized carbon nanotubes, wherein

(i) the functional groups are derivatized to the carbon nanotubes utilizing a diazonium specie and

(ii) the functional groups are capable of polymerizing; and

(b) polymerizing the derivatized carbon nanotubes to grow polymer from the functional groups.

125. The method of claim 124, wherein the carbon nanotubes are single-wall carbon nanotubes.

126. The method of claims 124 or 125, wherein the polymerization step comprises a technique selected from the group consisting of radical, cationic, anionic, condensation, ring-opening, methathesis, and ring-opening-metathesis (ROMP) polymerizations.

127. A polymer material made by the process comprising:

(a) derivatizing carbon nanotubes with functional groups to form derivatized carbon nanotubes, wherein

(i) the functional groups are derivatized to the carbon nanotubes utilizing a diazonium specie and

(ii) the functional groups are capable of polymerizing; and

(b) polymerizing the derivatized carbon nanotubes to grow polymer from the functional groups.

128. The polymer material of claim 127, wherein the carbon nanotubes are single-wall carbon nanotubes.

129. The polymer material of claims 127 or 128, wherein the polymerization step comprises a technique selected from the group consisting of radical, cationic, anionic, condensation, ring-opening, methathesis, and ring-opening-metathesis (ROMP) polymerizations.

Figure 1

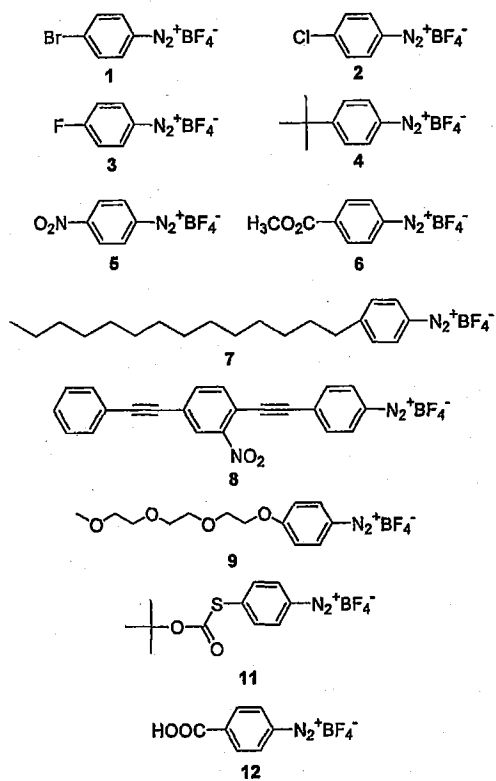
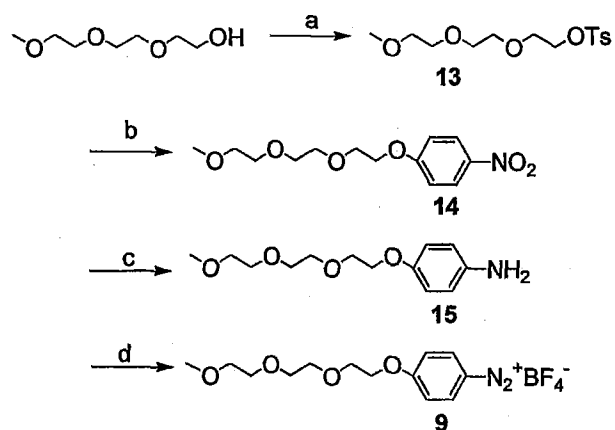


Figure 2



a) TsCl , H_2O , THF b) 4-nitrophenol,
 DMF , K_2CO_3 c) H_2 , Pd/C d) NOBF_4 ,
 CH_3CN

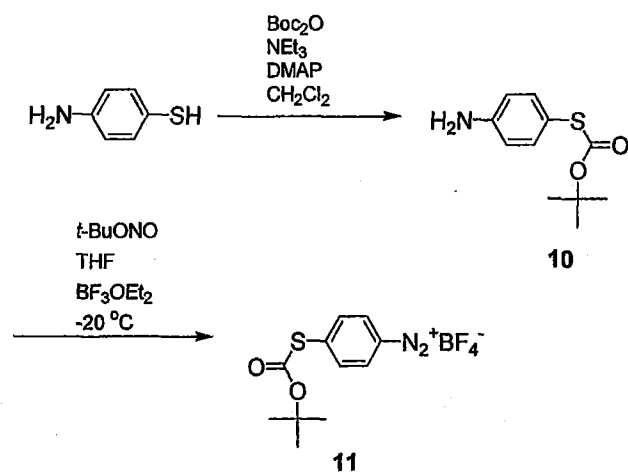


Figure 3

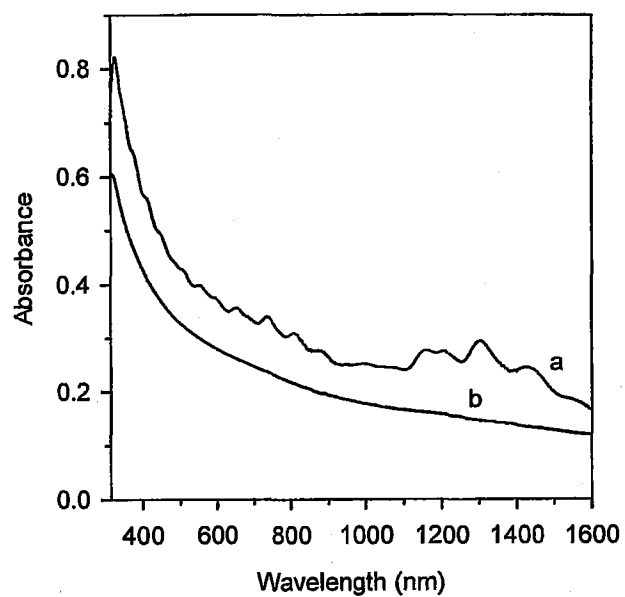


Figure 4

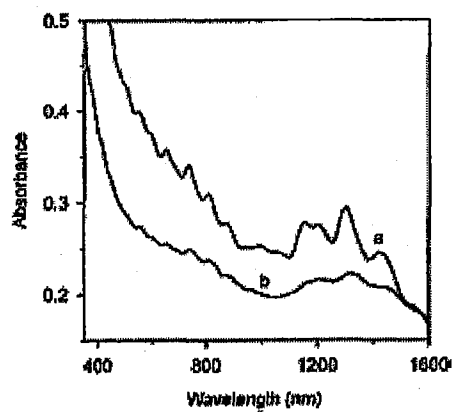


Figure 5

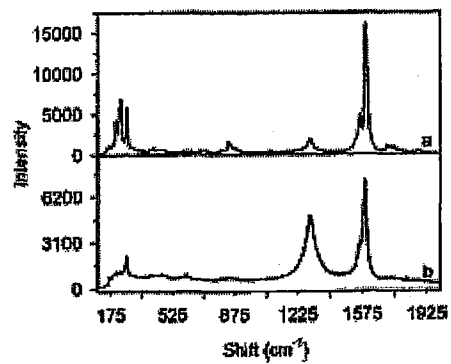


Figure 6

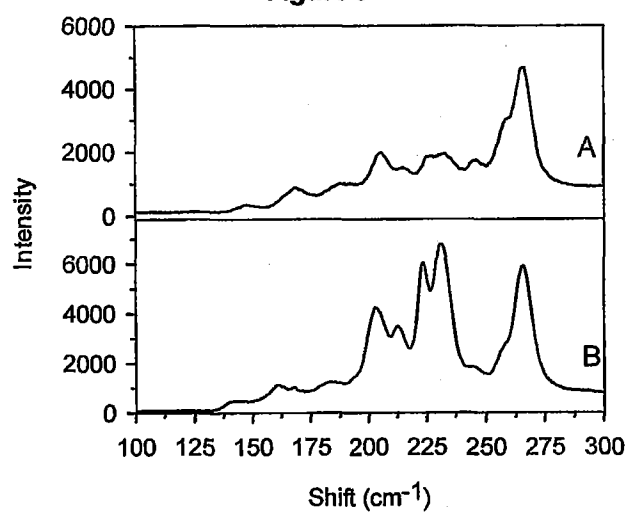


Figure 7

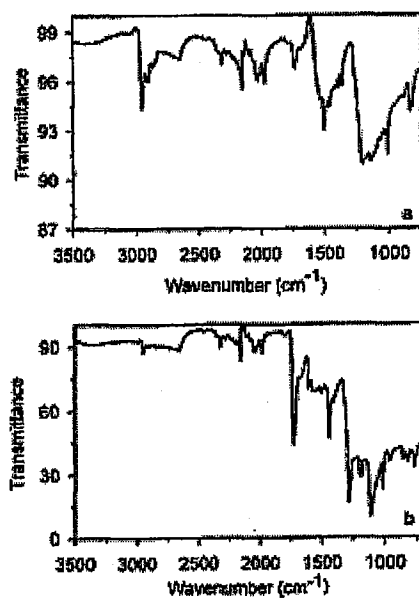


Figure 8

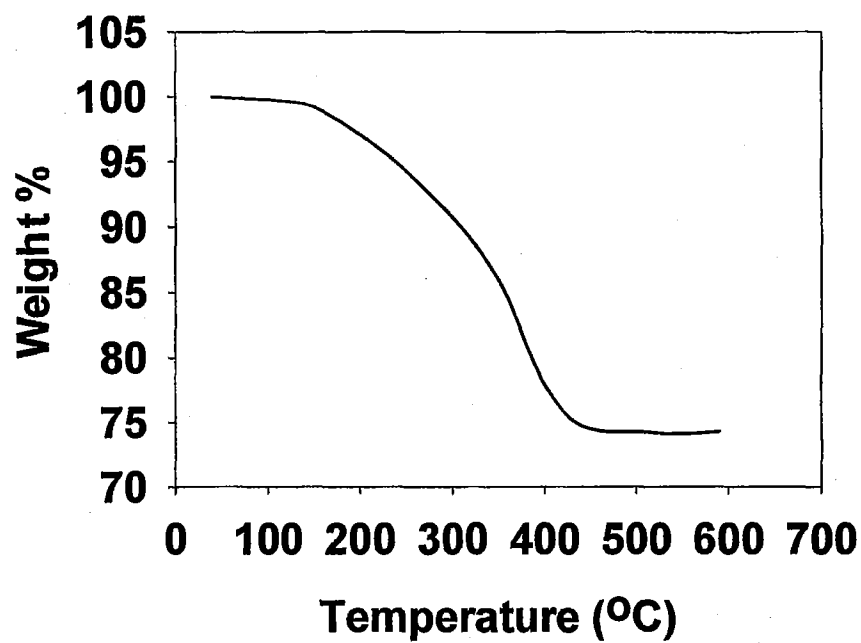


Figure 9

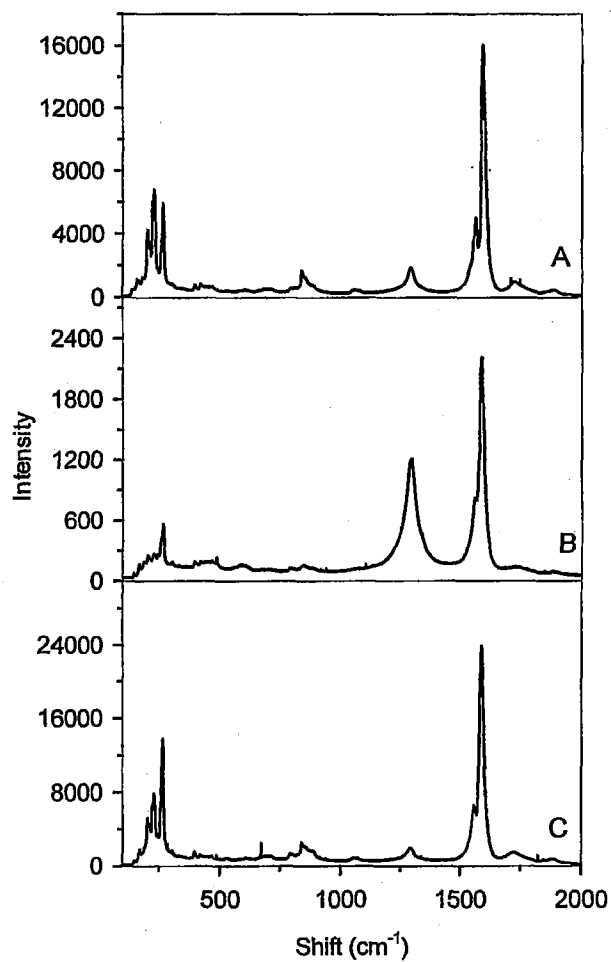


Figure 10

A

Figure 11

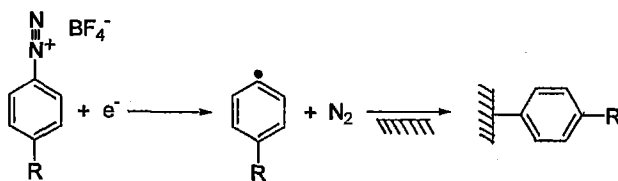
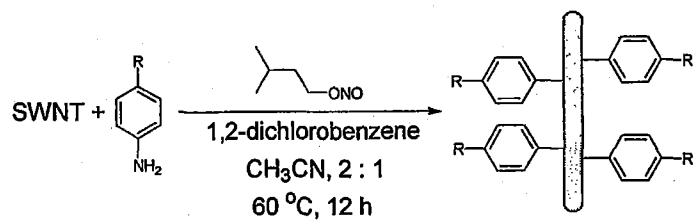


Figure 12



16, R = Cl

17, R = *tert*-butyl18, R = CO₂CH₃19, R = NO₂

20, R = COOH

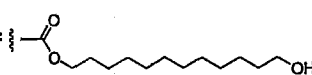
 21, R = 

Figure 13

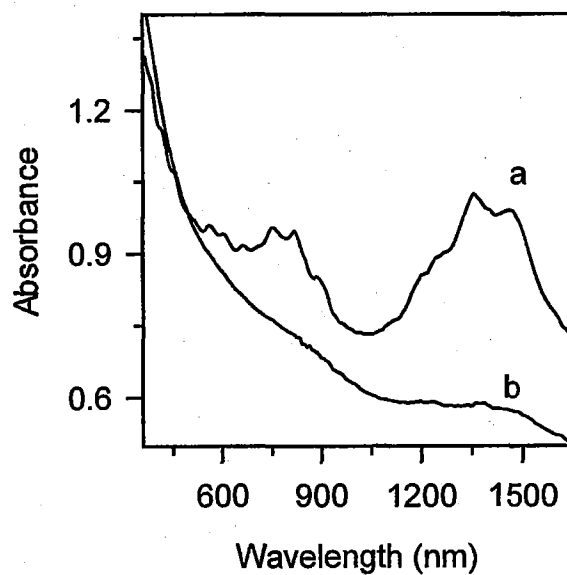


Figure 14

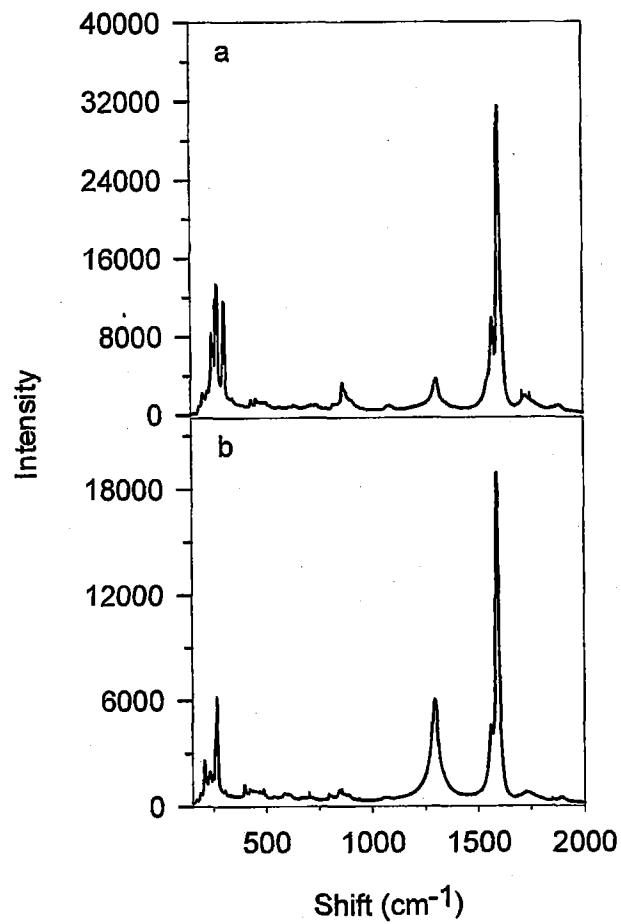


Figure 15

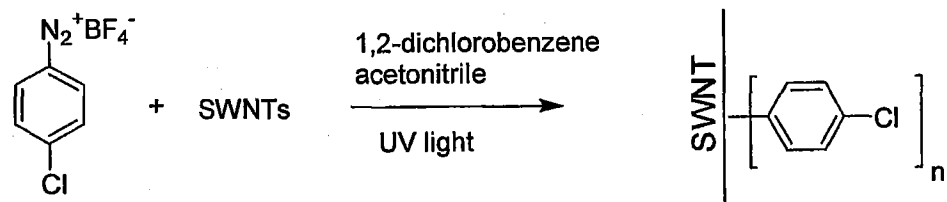


Figure 16

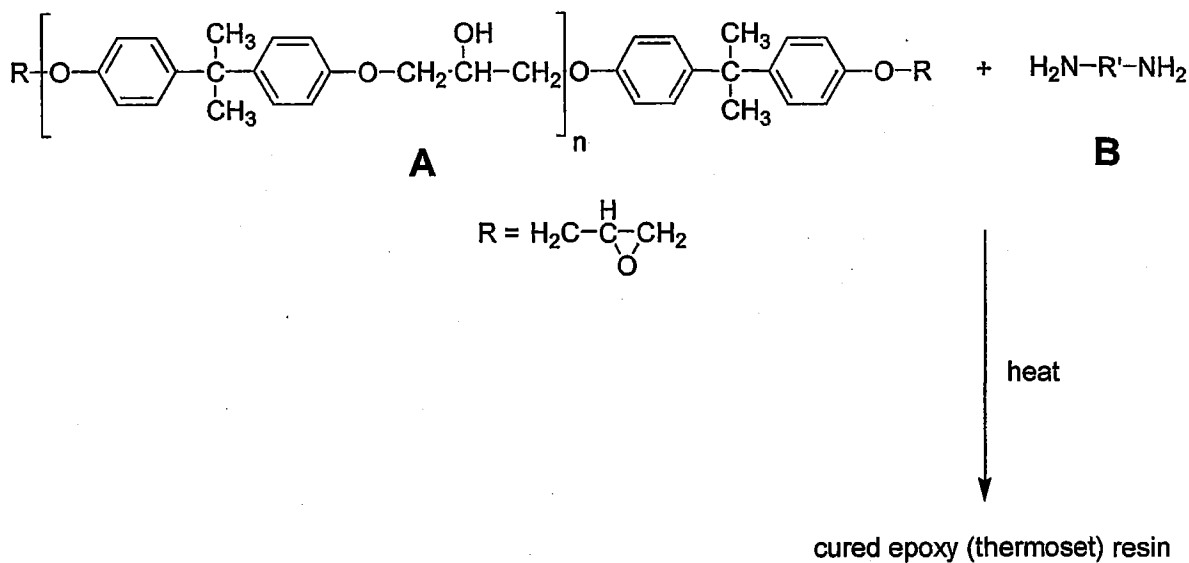


Figure 17

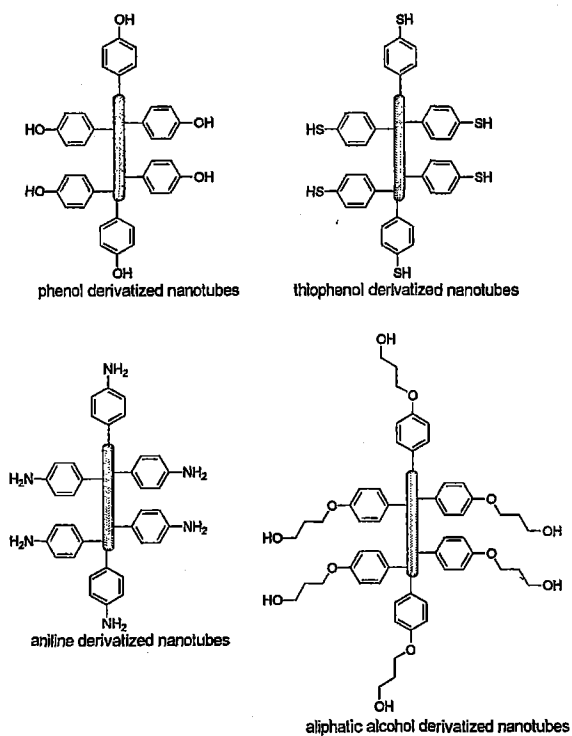


Figure 18

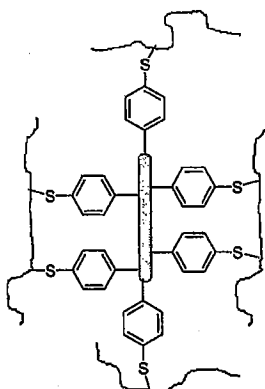


Figure 19

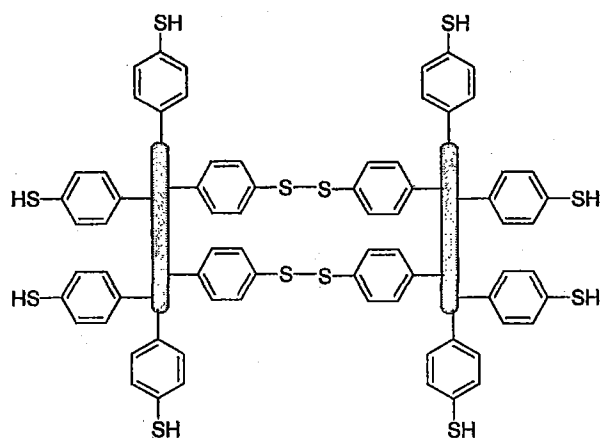


Figure 20

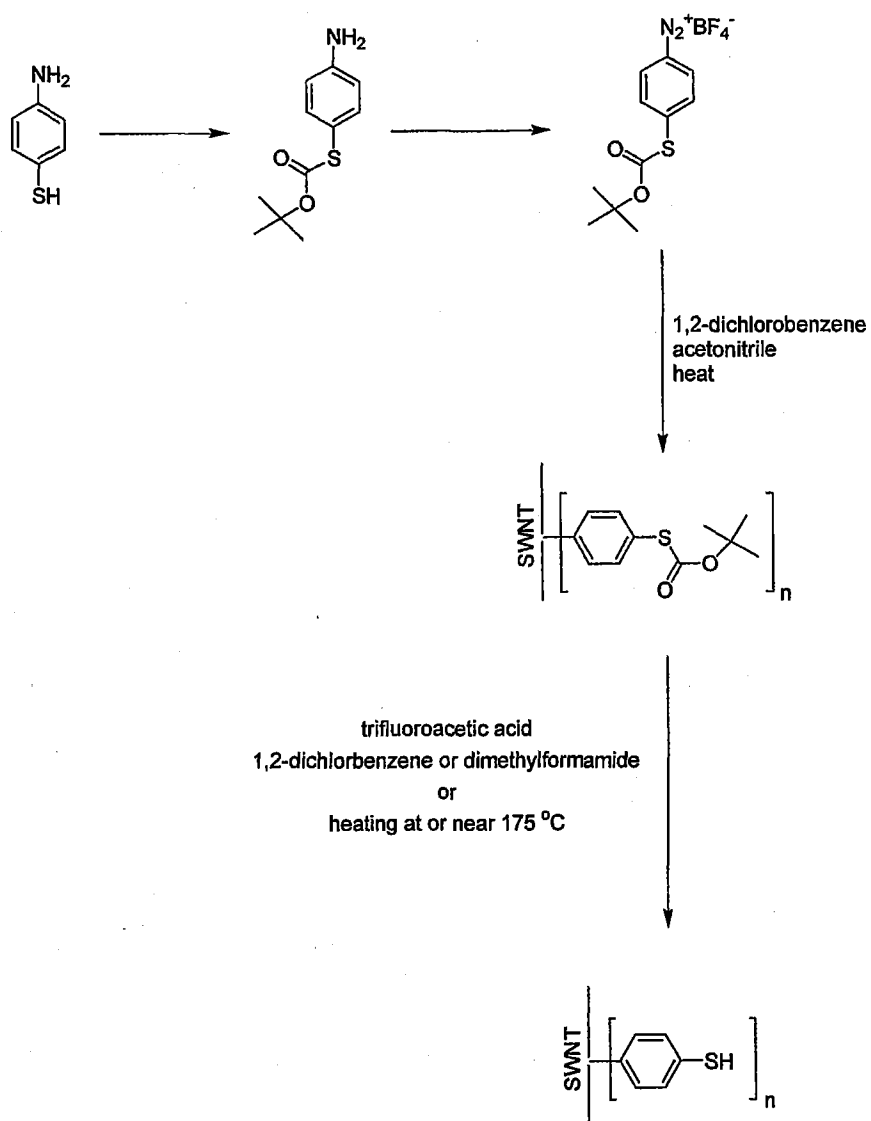


Figure 21

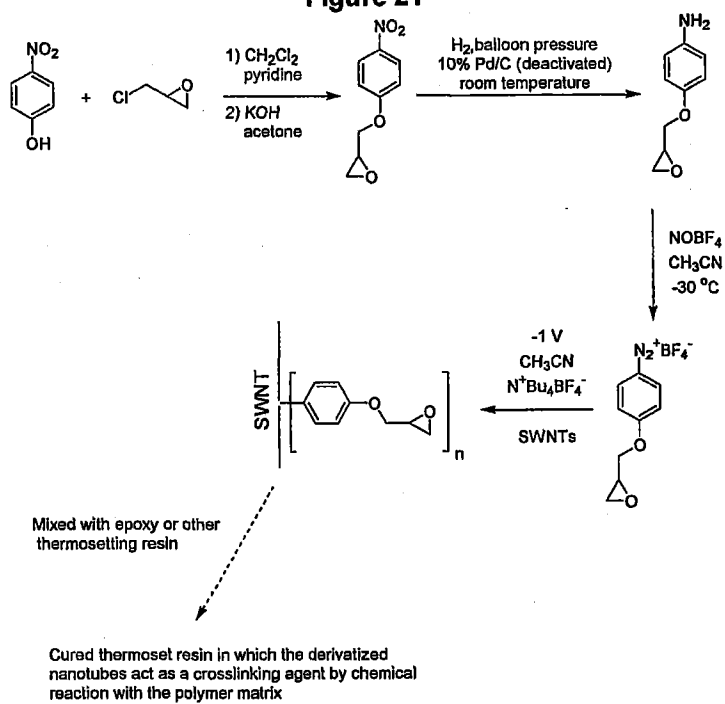


Figure 22

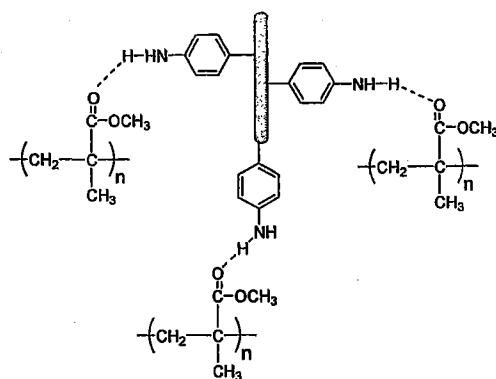
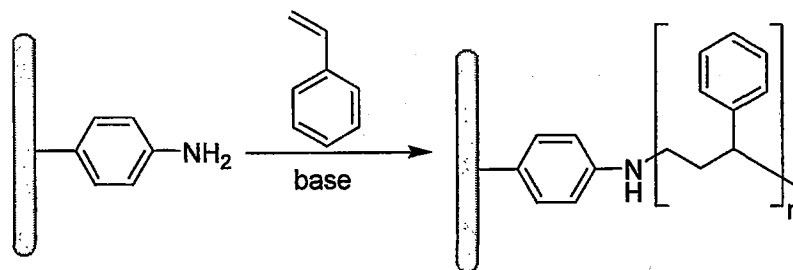


Figure 23



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3,554,992

POLYMERISATION CATALYSTS AND USES THEREOF

Donald Charles Lamb, Norton-on-Tees, England, assignor to Imperial Chemical Industries Limited, London, England, a corporation of Great Britain

No Drawing. Filed Mar. 25, 1968, Ser. No. 715,523
Claims priority, application Great Britain, Apr. 11, 1967,
16,475/67; Oct. 2, 1967, 44,775/67

Int. Cl. C08f 3/38, 15/10

U.S. Cl. 260-91.1

7 Claims

ABSTRACT OF THE DISCLOSURE

A novel catalyst for vinyl ether homo or heteropolymerisation comprises a Grignard complex $RXMg(hal)$ mounted on or in a solid support. R is a hydrocarbon group such as phenyl or an alkyl group, (hal) is a halogen and X is oxygen, sulphur, selenium or tellurium or is introduced by reacting a Grignard reagent $RMg(hal)$ with a compound containing an unsaturated linkage between different elements or with an olefine oxide. Preferably X is O or CO_2 and the complex may be formed in situ on the support. In the polymerisation the vinyl ether with or without other unsaturated monomers is contacted in the liquid phase with the catalyst, preferably in continuous fashion with a bed or column of the catalyst.

The present invention relates to a new polymerisation catalyst, a method for its preparation, and to its use in polymerising ethylenically unsaturated monomers, particularly vinyl ethers.

Vinyl ethers, especially alkyl vinyl ethers, are by virtue of their ethylenic unsaturation useful as polymerisable monomers. In addition the alkyl group and the ether linkage confer valuable properties on the polymers produced. Thus homopolymers of alkyl vinyl ethers may be used in the formulation of adhesives, lubricants and greases and surface coatings. Heteropolymers with other monomers such as styrene find outlets for example in the manufacture of clear moulding resins of high impact strength. The most important alkyl vinyl ethers for such applications are methyl vinyl ether, ethyl vinyl ether and isobutylvinyl ether although higher vinyl ethers such as laurylvinyl ether and isodecyl vinyl ether are also used.

Although the polymers possess such useful and valuable properties as those listed above, the development of vinyl ether polymers has been restricted by difficulties experienced in their polymerisation. Acid initiated polymerisation has been found to be the most effective technique but it is accompanied by certain disadvantages. For example the presence of trace impurities of high dielectric constant such as water can affect the rate of chain propagation and induce termination of the polymer chain. The alkyl vinyl ether monomers are also very reactive under acid conditions and often polymerise with explosive violence. This danger compels the polymerisation to be carried out at low temperatures, e.g. $-40^\circ C.$, particularly when high molecular weight polymers are required which among other difficulties tends to produce polymers with an undesirable proportion of crystallinity. Another disadvantage of the acid catalysts is the difficulty in removing them from the polymers after the polymerisation. Acid catalyst residues left in the polymer are capable of causing chain scission and depolymerisation.

We have now found a catalyst which avoids many of the above disadvantages. In particular the polymerisation can be carried out without the need for refrigeration and the finished polymer is readily separable from the catalyst.

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According to the invention a novel catalyst for the homopolymerisation of a vinyl ether or the heteropolymerisation of a vinyl ether with another ethylenically unsaturated monomer comprises a Grignard complex of formula:



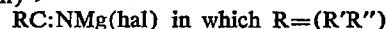
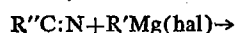
contained on or in a solid support.

In the formula $RXMg(hal)$ R is an alkyl, cycloalkyl, aryl, alkaryl, aralkyl or a heterocyclic group, (hal) is chlorine, bromine or iodine and X represents oxygen, sulphur selenium or tellurium or is a group introduced by the reaction of a Grignard reagent $R'Mg(hal)$ (in which R' is a hydrocarbon group) with an olefine oxide or a compound containing an unsaturated linkage between different elements. In such reactions the group R' attaches to the relatively less acid element and the group Mg(hal) to the relatively more acidic element.

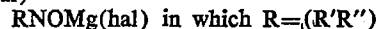
In the Grignard reagent $R'Mg(hal)$ R' is a hydrocarbon group which may be alkyl, cycloalkyl, e.g. cyclohexyl, aryl, alkaryl, aralkyl or a heterocyclic group. Phenyl or alkyl substituted phenyl groups, such as tolyl, or alkyl groups containing up to 10 carbon atoms are preferred. Suitably R' may be phenyl, tolyl, benzyl, methyl, ethyl, propyl, butyl, amyl or hexyl.

The compound containing an unsaturated linkage may be organic or inorganic in nature. For example:

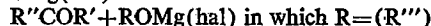
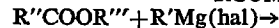
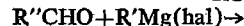
(a) Nitriles, e.g. aliphatic nitriles such as acetonitrile and propionitrile and aromatic nitriles such as benzonitrile, the reaction being:



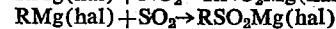
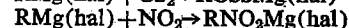
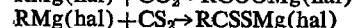
(b) Nitroso compounds, principally aromatic nitroso compounds such as nitrosobenzene. The reaction in this case is:



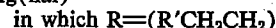
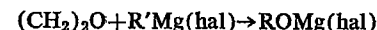
(c) Aldehydes, ketones or esters, in which the unsaturated linkage is between carbon and oxygen. The aldehyde, ketone or ester may be aliphatic or aromatic in nature e.g. alkanals or alkanones containing up to 12 carbon atoms e.g. acetone, acetaldehyde, methyl ethyl ketone and heptaldehyde. Suitable esters include those of the lower fatty acids e.g. acetic acid esters. For example:



Among the inorganic compounds containing an unsaturated linkage which may be used are carbon dioxide, carbon disulphide, nitrogen dioxide, nitric oxide and sulphur dioxide, the reaction being:



Olefine oxides which may be used include ethylene and propylene oxides. The reaction being e.g.:



Examples of R in the Grignard complex are cyclohexyl, phenyl, benzyl or tolyl. Preferably R is an alkyl group, more preferably an alkyl group containing up to 20 carbon atoms, for example, methyl ethyl, propyl, butyl, amyl, nonyl, decyl, lauryl, pentadecyl or octadecyl.

Chlorine and bromine are the preferred halogens, principally because of the ready availability of Grignard complexes containing them.

The solid support is inert and serves only to carry the Grignard complex. The complex may be contained on the surface of the support, or in the pores and interstices of a microporous support. Suitable supports include stainless steel helices ceramics such as earthenware and porcelain, alumina, asbestos, charcoal and silica. The support may be in any convenient physical form but is preferably selected so as to expose the greatest internal and/or external surface area on which the Grignard complex may be carried. When the support is a ceramic it may advantageously be used in bead or ring form.

The Grignard complex is most readily formed in situ on the support. This may be accomplished by first coating the support with the Grignard reagent $\text{RMg}(\text{hal})$ and then treating the coated support with one of the reactants described above e.g. oxygen or carbon dioxide, which give rise to preferred forms of the Grignard complex.

Thus ceramic rings or beads or stainless steel helices may be soaked in a solution containing an alkyl magnesium chloride or bromide. Evaporation of the solvent by carbon dioxide or air blowing of the coated rings, beads or helices yields the desired catalyst i.e. (alkyl) $\text{OMg}(\text{hal})$ or (alkyl) $\text{COOMg}(\text{hal})$ deposited on the support. Preferably the solvent from which the Grignard reagent is deposited is di-ethyl ether.

In some instances it may be advantageous to heat the complex after its formation to alter its selectivity in the polymerisation of vinyl ethers. For example if



is heated to a temperature of 65°C . after its formation it is more active for the polymerisation of methyl vinyl ether than for isobutyl vinyl ether. Generally the complex may be heated up to 300°C . preferably up to 250°C . If the complex is not heated its activity is different being more active in polymerising isobutyl vinyl ether than methyl vinyl ether.

The catalysts of the present invention may be used to polymerise vinyl ethers either alone or with an ethylenically unsaturated comonomer. The most important vinyl ethers are the alkyl vinyl ethers particularly alkyl vinyl ethers in which the alkyl group contains up to 20 carbon atoms. Examples of such ethers are methyl vinyl ether, ethyl vinyl ether, isobutyl vinyl ether, lauryl vinyl ether and isodecyl vinyl ether.

Ethylenically unsaturated monomers which may be polymerised with the vinyl ethers include styrene, maleic anhydride, acrylonitrile, vinyl chloride, acrylate esters and similar monomers which do not contain active groups which may deactivate the catalyst.

The polymerisation process is carried out in the liquid phase preferably at a temperature in the range 20°C to 100°C . It is convenient to use an inert solvent to bring the vinyl ether and other monomer (if one is used) into contact with the catalyst. Suitable solvents are hydrocarbon solvents particularly aromatic hydrocarbon solvents such as benzene and toluene or alkane solvents such as hexane or polar solvents such as di-ethyl ether and methylene chloride. The monomers preferably form 25 to 75% by weight of the solution and in a batch process the weight percent of the catalyst used is preferably 0.5 to 5, more preferably 0.5 to 1.0 (the percentage figures refer to the weight of $\text{RXMg}(\text{hal})$ not to the weight of the Grignard complex plus support).

Although in general the polymerisation is conducted at ambient pressure, for the lower boiling ethers elevated pressure e.g. up to 50 atmospheres may be used. For example methyl vinyl ether was polymerised in the presence of $\text{C}_4\text{H}_9\text{OMgBr}$ at a pressure of 20 atmospheres.

The polymerisation may also be carried out in a continuous manner by passing a solution of the monomer(s) over a bed or through a column packed with the catalyst.

The polymer may be recovered from the solution leaving the bed or column by distilling off the solvent and excess monomer or by precipitating the polymer with for example methanol. For some applications e.g. adhesives, the polymer solution may be used directly. The continuous process is particularly advantageous because the heat of reaction may be removed by the solution flowing over the catalyst and because the separation of catalyst and polymer solution does not require a separate step.

The invention will now be further described by reference to the following examples.

EXAMPLE 1

Catalyst preparation

(1a) Dry magnesium turnings (8.9 grams) and dry di-ethyl ether (50 mls.) were placed in a round-bottomed flask fitted with a stirrer and a condenser cooled by solid carbon dioxide. The flask was purged with argon. n-Bromobutane (50 grams) in di-ethyl ether (100 grams) was then added dropwise to the reaction vessel over a period of 30 minutes. The reaction vessel was cooled by means of a water bath so that a gentle reflux rate was maintained.

When the reaction was complete ceramic beads were soaked in the ethereal Grignard solution and air blown causing the catalyst to be precipitated. The coated beads were then packed into a column.

Alternatively the column was packed with ceramic beads and the Grignard solution run down the column. Air was blown up the column thereby precipitating the catalyst in situ.

(1b) Catalysts were prepared in similar fashion to the above using fired alumina pellets and stainless steel helices instead of ceramic beads. By blowing with carbon dioxide instead of air catalysts containing n-butyl carboxy magnesium bromide were obtained.

Polymerisation

(2) A 50% solution of isobutyl vinyl ether in toluene was pumped through a water jacketed column prepared as described above containing ceramic beads coated with n-butyloxymagnesium bromide. Water at 50°C . was circulated through the column. The polymer formed was precipitated from solution by ammoniacal methanol.

A column packed with precoated ceramic beads still gave satisfactory polymerisation after 66 hours while the column coated in situ as described above still gave satisfactory polymerisation after 41½ hours.

EXAMPLE 2

Catalyst preparation

(1) A water jacketed column maintained at 30°C . was packed with α -alumina pellets and a 20% ethereal solution of n-butylmagnesium bromide run down it. Sulphur dioxide was then blown up the column precipitating the complex $\text{C}_4\text{H}_9\text{SO}_2\text{MgBr}$ on the pellets.

Polymerisation

(2) Methyl vinyl ether was passed through the column prepared as in (1) above and collected from the top of the column in a reservoir. Samples were taken of the reservoir contents at regular intervals and 10 ml. of methanol was added to each sample to destroy any catalyst which might be present. The sample was then heated at 65°C . under vacuum (2 mm. mercury) for 15 minutes. The weight of polymer collected was recorded.

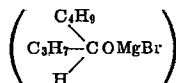
	Reaction times, minutes	Weight of polymer produced, grams
Sample:		
1.....	30	5½
2.....	60	2½
3.....	90	1¾

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The following experiments are illustrative of the range of Grignard complexes which when contained on or in a solid support form the catalysts of the present invention. Although the Grignard complex may be used without the support, as is described below, this method is inferior, particularly in the operation of a continuous commercial process to the supported catalyst of the present invention.

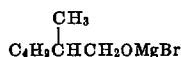
(a) 18 grams of bromobenzene were slowly added to 3 grams of magnesium turnings in 100 grams of refluxing diethyl ether. Solid carbon dioxide was then added to the cooled ethereal solution, the ether removed, and the product $C_6H_5CO_2MgBr$ dried under vacuum at $50^\circ C.$ for 2 hours. 5 grams of the complex were added to 53 grams of isobutyl vinyl ether and 50 grams of toluene and the mixture heated at $50^\circ C.$ for 2 hours. The yield of polyisobutyl vinyl ether was 91% of the theoretical.

(b) A 20% solution of isobutyl magnesium bromide in ether was prepared by a similar technique to that used in Example 1. Stoichiometric amounts of this complex and isobutyraldehyde were reacted together and 1 gram of the complex so formed:



added to 8 grams of isobutyl vinyl ether, the mixture being maintained at a temperature of $20^\circ C.$ for 100 hours. The yield of polyisobutyl vinyl ether was 96% of the theoretical.

(c) Experiment (b) was repeated replacing the isobutyraldehyde by propylene oxide. The complex obtained was



and the yield of polyisobutyl vinyl ether was 48% of the theoretical.

(d) 20 mls. of a 20% solution of n-butyl magnesium bromide, prepared as in Example 1, was reacted with 30 mls. of liquid sulphur dioxide at $-40^\circ C.$ The product, $n-C_4H_9SO_2MgBr$, was dried at $65^\circ C.$ under vacuum for $1\frac{1}{2}$ hours. Half a gram of the complex was sealed in a vial with 10 mls. methyl vinyl ether for 16 hours at $30^\circ C.$ to yield a colourless clear soft polymer.

(e) Experiment (d) was repeated replacing the liquid sulphur dioxide by liquid nitrogen dioxide. After 2 days at $30^\circ C.$ 0.5 gram of the complex ($n-C_4H_9NO_2MgBr$) polymerised 8.0 grams of isobutyl vinyl ether.

(f) 20 mls. of a 20% solution of $n-C_4H_9CO_2MgBr$ in di-ethyl ether was added to 30 mls. of carbon disulphide at $-40^\circ C.$ The resulting complex $n-C_4H_9CS_2MgBr$ was dried under vacuum at $65^\circ C.$ for 90 minutes. 0.5 gram of this complex polymerised 8.0 grams of isobutyl vinyl ether in 3 days at $30^\circ C.$

(g) A stoichiometric excess (24 grams) of n-butyl-acrylate was added to 12.5 mls. of a 20% $n-C_4H_9MgBr$ solution in di-ethyl ether prepared as in Example 1. A further 50 mls. of di-ethyl ether and 36 grams of isobutyl vinyl ether were added and the solution heated at $50^\circ C.$

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for $2\frac{1}{2}$ hours. The polymer obtained was dried and found to weigh 46 grams.

(h) 50 mls. of a 20% solution of n-butyl magnesium bromide prepared as in Example 1, 100 mls. n-hexane and 50 mls. of isobutyl vinyl ether were heated to $50^\circ C.$ 30 mls. of isobutyl vinyl ether and 30 mls. of isobutyraldehyde were added to the solution over a period of 2 hours and the reaction mixture allowed to stand for 3 days. The polymer was dried and found to weigh 65 grams.

I claim:

1. A process for the homopolymerization of an alkyl vinyl ether containing up to 20 carbon atoms in the alkyl group or the heteropolymerization of said vinyl ether with another ethylenically unsaturated monomer selected from the group consisting of styrene, maleic anhydride, acrylonitrile, vinyl chloride and acrylate esters which comprises contacting in a liquid phase said ether or said ether and said monomer with a catalytic amount of a catalyst which comprises a Grignard complex of formula $RXMg(hal)$ and an inert support therefor in which R is an alkyl, cycloalkyl, aryl, alkaryl, aralkyl or a heterocyclic group (hal) is chlorine, bromine or iodine and X is selected from the group consisting of O, S, Se, Te, C, N, NO, CO, COO, CSS, NO_2 and SO_2 .

2. The process of claim 1 in which R is cyclohexyl, phenyl, benzyl, tolyl or an alkyl group containing up to 20 carbon atoms.

3. The process of claim 1 in which the inert catalyst support is selected from the group consisting of stainless steel helices, earthenware, porcelain, alumina, asbestos, silica and charcoal.

4. The process of claim 1 in which the catalyst is heated before the polymerization to a temperature of up to $300^\circ C.$

5. The process of claim 1 in which a temperature in the range 20° to $100^\circ C.$ is used.

6. The process of claim 1 in which a solvent is present.

7. The process of claim 1 in which said alkyl vinyl ether is continuously passed in solution in an aromatic hydrocarbon solvent or in diethyl ether or methylene chloride over a bed or through a column of a Grignard complex of Formula $RXMg(hal)$ contained on or in a solid inert support, in which R is phenyl, benzyl, tolyl, methyl, ethyl, propyl, butyl or amyl, X is NO_2 , SO_2 , CS_2 , O or CO_2 and (hal) is chlorine or bromine.

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HARRY WONG, JR., Primary Examiner

U.S. Cl. X.R.

252—431; 260—78.5, 80.3, 85.5, 86.1, 87.5, 88.1



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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/561,253	12/19/2005	James M. Tour	11321-P068WOUS	6532
<div>7590 04/06/2010 Robert C Shaddox Winstead Sechrest Minick PO Box 50784 Dallas, TX 75201</div>			<div>EXAMINER CHEUNG, WILLIAM K</div>	
			<div>ART UNIT 1796</div>	<div>PAPER NUMBER</div>
			<div>MAIL DATE 04/06/2010</div>	<div>DELIVERY MODE PAPER</div>

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary

Application No.

10/561,253

Applicant(s)

TOUR ET AL.

Examiner

WILLIAM K. CHEUNG

Art Unit

1796

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 03 February 2010.
- 2a) ☒ This action is **FINAL**. 2b) ☐ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 2-6,8-28 and 31-34 is/are pending in the application.
- 4a) Of the above claim(s) _____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 2-6,8-28 and 31-34 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
 2. ☐ Certified copies of the priority documents have been received in Application No. _____.
 3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- | | |
|--|---|
| 1) <input type="checkbox"/> Notice of References Cited (PTO-892) | 4) <input type="checkbox"/> Interview Summary (PTO-413) |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948) | Paper No(s)/Mail Date. _____ |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO/SB/08) | 5) <input type="checkbox"/> Notice of Informal Patent Application |
| Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____ |

DETAILED ACTION

1. In view of the amendment filed February 3, 2010, claims 1, 7, 29, 30 have been cancelled. Claims 2-6, 8-28, 31-34 are pending.

Claim Rejections - 35 USC § 103

2. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

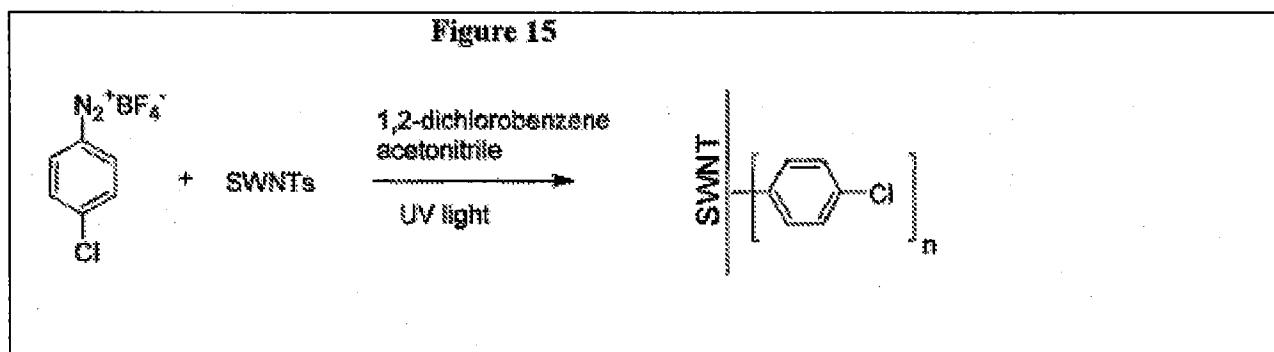
The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.
 2. Ascertaining the differences between the prior art and the claims at issue.
 3. Resolving the level of ordinary skill in the pertinent art.
 4. Considering objective evidence present in the application indicating obviousness or nonobviousness.
3. Claims 2-6, 8-28, 31-34 are rejected under 35 U.S.C. 103(a) as being unpatentable over Tour et al. (WO 02/060812) in view of Lamb et al. (US 3,554,992) for the reasons adequately set forth from paragraph 4 of the office action of June 17, 2009.

2. (Previously Amended) A method comprising:
- a) providing aryl halide functionalized carbon nanotubes;
wherein the aryl halide comprises a halide selected from the group consisting of chlorine, bromine, iodine, and combinations thereof;
 - b) dispersing the aryl halide functionalized carbon nanotubes in a solvent;
 - c) adding an alkyl lithium species to the solvent,
wherein the alkyl lithium species reacts with the aryl halide functionalized carbon nanotubes to form an aryl-lithium species;
wherein the aryl-lithium species comprises a polymerizable species on the carbon nanotubes; and
wherein the polymerizable species comprises aryl-lithium covalent bonds;
 - d) adding a monomer to the solvent; and
 - e) initiating a polymerization reaction between the monomer and the polymerizable species to form a polymer-carbon nanotube material,
wherein a polymer comprising the polymer-carbon nanotube material is covalently bound to the carbon nanotubes; and
wherein the polymerization reaction is selected from the group consisting of anionic polymerization and ring opening polymerization.
3. (Previously Amended) A method comprising:
- a) providing aryl halide functionalized carbon nanotubes;
wherein the aryl halide comprises a halide selected from the group consisting of chlorine, bromine, iodine, and combinations thereof;
 - b) dispersing the aryl halide functionalized carbon nanotubes in a solvent;
 - c) adding a metal to the solvent,
wherein the metal reacts with the aryl halide functionalized carbon nanotubes to form an aryl-metal species;
wherein the aryl-metal species comprises a polymerizable species on the carbon nanotubes; and
wherein the polymerizable species comprises aryl-metal covalent bonds;
 - d) adding a monomer to the solvent; and
 - e) initiating a polymerization reaction between the monomer and the polymerizable species to form a polymer-carbon nanotube material,
wherein a polymer comprising the polymer-carbon nanotube material is covalently bound to the carbon nanotubes; and
wherein the polymerization reaction is selected from the group consisting of anionic polymerization and ring opening polymerization.

10. (Previously Amended) A method comprising:
- providing functionalized carbon nanotubes,
wherein the functionalized carbon nanotubes comprise nucleation sites operable for initiating a polymerization reaction after deprotonation of said nucleation sites to form initiator groups;
wherein the polymerization reaction is selected from the group consisting of anionic polymerization and ring opening polymerization;
 - dispersing the functionalized carbon nanotubes in a solvent;
 - adding a deprotonating agent to the solvent,
wherein the deprotonating agent deprotonates the nucleation sites to form initiator groups operable for initiating the polymerization reaction;
 - adding a monomer to the solvent; and
 - initiating a polymerization reaction between the monomer and the initiator groups to form a polymer-carbon nanotube material,
wherein a polymer comprising the polymer-carbon nanotube material is covalently bound to the carbon nanotubes; and
wherein the polymerization reaction is selected from the group consisting of anionic polymerization and ring opening polymerization.

Tour et al. (page 8/12 of figures, Figure 15) disclose the preparation of single-wall carbon nano-tube (SWNT) functionalized with aryl chlorine containing functionality.



Then, Tour et al. (page 2, line 13-18) disclose halogenated SWNT can participate reactions with alkyl-lithium reagent (via Grignard reaction mechanism). Further, Tour et

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al. (page 31, claims 125-129) disclose that the functionalize SWNT can undergo various polymerization mechanisms that includes anionic polymerization.

Regarding claim 10 which recites "operable for anionic or ring opening polymerization", in view of the substantially identical SWNT disclosed in Tour et al. and as claimed, the examiner has a reasonable basis that the "operable" feature is inherently possessed in Tour et al.

Regarding claim 33 which recites "the step of utilizing the polymer-carbon nanotube material in a drug delivery process" or regarding claim 34 which recites "the step of utilizing the polymer-carbon nanotube material for scaffolding to promote cellular tissue", the recitations are merely related to the intended use of the claimed process, applicants must recognize that a recitation of the intended use of the claimed invention must result in a structural difference between the claimed invention and the prior art in order to patentably distinguish the claimed invention from the prior art. If the prior art structure is capable of performing the intended use, then it meets the claim.

The difference between Tour et al. and the invention as claimed is that Tour et al. do not teach the specific mechanism for preparing a polymer.

However, Lamb et al. (col. 3, line 14 to col. 4, line 75) clearly disclose the specifics for using a Grignard reaction for initiating a polymerization process. Lamb et al. (col. 3, line 41-53) disclose the types of monomers that are suitable for the polymerization process as claimed. Lamb et al. (col. 3, line 54-67) disclose the use of ethereal solvents and hydrocarbon solvents for the polymerization process. Although Lamb et al. do not specifically indicate the use of THF as one of the ethereal solvent,

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however, it would not be difficult to one of ordinary skill in art recognize and appreciate that THF is also an ethereal solvent. (see http://en.wikipedia.org/wiki/Grignard_reaction)

Regarding the claimed "terminating agents" of claims 25, 26, Lamb et al. (col. 4, line 44) clearly disclose the use of methanol for precipitating the polymers from the solution, the examiner has a reasonable basis that one of ordinary skill in art would have recognize that the disclosed "method" is a terminating agent, and that other organic alcohols, such as ethanol would also be a functional equivalence of the disclosed methanol terminating agent. (see http://en.wikipedia.org/wiki/Grignard_reaction)

Regarding the concentration feature of claim 27, and the temperature feature of claim 28, the mere variation of concentration and temperature are considered obvious because it is within the skill of one of ordinary skill in art to apply "routine optimization" process to optimize that concentration and temperature conditions of a polymerization process, motivated by the expectation of increasing the yield or the improving the quality of the polymer products.

Motivated by the expectation of success of preparing a polymer with a Grignard reagent, it would have been obvious to one of ordinary skill in art to incorporate all reaction related specifics as taught in Lamb et al. into Tour et al. to obtain the invention as claimed.

Regarding the "deprotonating agent" of claims 14-15, the variation of concentration of claim 27, and the polymerization temperature of claim 28, Tour et al. (page 2, line 13-18) clearly disclose that halogenated SWNT can participate reactions

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with alkyl-lithium reagent (via Grignard reaction mechanism). Further, Tour et al. (page 31, claims 125-129) disclose that the functionalize SWNT can undergo various polymerization mechanisms that includes anionic polymerization. The minor variation of the reaction conditions of an explicitly taught polymerization route is considered obvious. Motivated by the expectation of success of developing a polymerization process using halogenated SWNT, it would have been obvious to one of ordinary skill in art to consult general information on Grignard reaction to obtain the polymerization conditions as claimed in claims 27, 28. (see http://en.wikipedia.org/wiki/Grignard_reaction)

Applicant's arguments filed February 3, 2010 have been fully considered but they are not persuasive. Applicants argue that the examiner has mischaracterized the reaction mechanisms of both Figure 1 and 2. However, the examiner disagrees because the examiner merely stated that the argued difference in reaction mechanism is not supported by the claims as written. The claims, as written, do not exclude or require any specific reaction mechanism, such as the SN2 reaction mechanism.

Applicants argue that Figure 1 presented in the last argument of September 17, 2009 (as shown below) is from the Margrave (US patent 6,827,918).

Figure 1

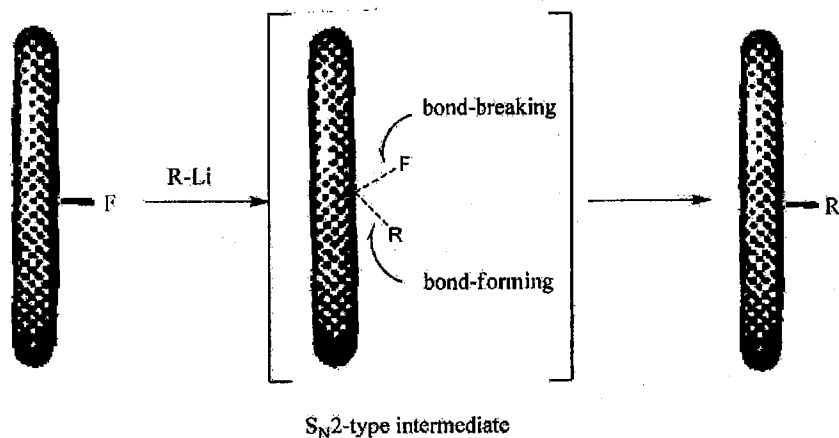
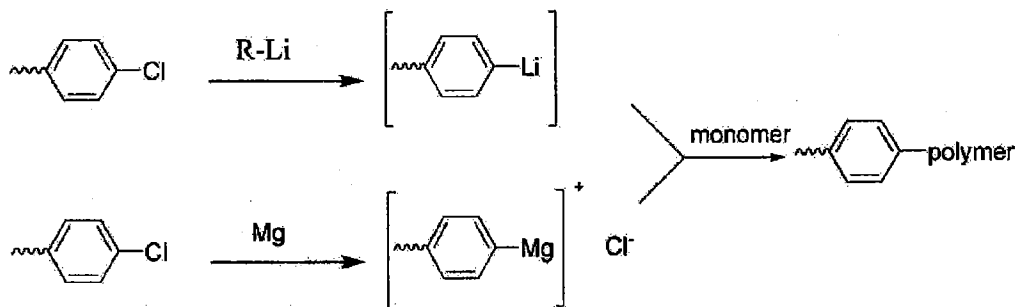


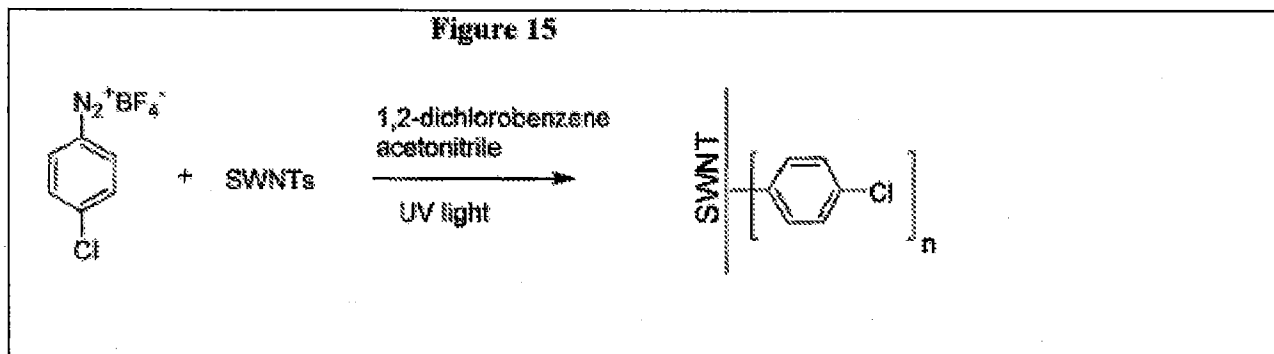
Figure 2



However, the examiner is unclear why applicants presented the Figure 1 of Margrave when the Margrave teach a reaction that is different from the reaction being taught in Tour et al. As taught, Tour et al. (page 8/12 of figures, Figure 15) disclose the preparation of single-wall carbon nano-tube (SWNT) functionalized with aryl chlorine containing functionality. Applicants must recognize that Figure 15 of Tour et al. does not

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resemble the reaction as argued by applicants' presented Figure 1, in that Tour et al. teach the formation of aryl halide while Figure 1 teaches the formation of alkylated carbon nanotube.



Because the Figure 1 of Margrave does not show a reaction that is similar to the reaction as taught in Tour et al., applicants' continued arguments based on the Figure 1 of Margrave is irrelevant to the 103 rejection set forth.

Therefore, in view of the reasons set forth above, applicants' argument that the examiner is mischaracterizing the reaction mechanisms of Tour et al. is unfounded. For the same reasons set forth above, applicants do not have any basis that the reaction mechanism of Tour et al. does not involve the reaction mechanism of a Grignard reaction or having a Grignard complex, etc. Applicants must not ignore the teachings of Tour et al., which is clearly shown in Figure 15 above, and Figure 15 teaches the formation of halogenated SWNT.

For the reasons above, the 103 rejection is maintained.

Conclusion

4. THIS ACTION IS MADE FINAL. Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to WILLIAM K. CHEUNG whose telephone number is (571)272-1097. The examiner can normally be reached on Monday-Friday 9:00AM to 2:00PM; 4:00PM to 8:00PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, David WU can be reached on (571) 272-1114. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

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Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/William K Cheung/
Primary Examiner, Art Unit 1796

William K. Cheung, Ph. D.
Primary Examiner
April 1, 2010



US006827918B2

(12) **United States Patent**
Margrave et al.

(10) **Patent No.: US 6,827,918 B2**
 (45) **Date of Patent: *Dec. 7, 2004**

(54) **DISPERSIONS AND SOLUTIONS OF
 FLUORINATED SINGLE-WALL CARBON
 NANOTUBES**

(75) **Inventors:** John L. Margrave, Bellaire, TX (US);
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 Smith, Spring, TX (US); Daniel T.
 Colbert, Houston, TX (US)

(73) **Assignee:** William Marsh Rice University,
 Houston, TX (US)

(*) **Notice:** Subject to any disclaimer, the term of this
 patent is extended or adjusted under 35
 U.S.C. 154(b) by 561 days.

This patent is subject to a terminal dis-
 claimer.

(21) **Appl. No.: 09/809,865**

(22) **Filed: Mar. 16, 2001**

(65) **Prior Publication Data**

US 2001/0031900 A1 Oct. 18, 2001

Related U.S. Application Data

(62) Division of application No. 09/787,473, filed as application
 No. PCT/US99/21366 on Sep. 17, 1999

*(60) Provisional application No. 60/101,092, filed on Sep. 18,
 1998, provisional application No. 60/106,918, filed on Nov.
 3, 1998, and provisional application No. 60/138,505, filed
 on Jun. 10, 1999.

(51) **Int. Cl.⁷ D01F 9/12**

(52) **U.S. Cl. 423/447.1**

(58) **Field of Search 423/447.1, 460**

(56) **References Cited**

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WO	WO 00/73205 A1	12/2000

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(List continued on next page.)

Primary Examiner—Stuart Hendrickson

(74) *Attorney, Agent, or Firm*—Ross Spencer Garsson;
 Robert C. Shaddox; Winstead Sechrest & Minick P.C.

(57) **ABSTRACT**

This invention is directed to making chemical derivatives of
 carbon nanotubes and to uses for the derivatized nanotubes,
 including making arrays as a basis for synthesis of carbon
 fibers. In one embodiment, this invention also provides a
 method for preparing single wall carbon nanotubes having
 substituents attached to the side wall of the nanotube by
 reacting single wall carbon nanotubes with fluorine gas and
 recovering fluorine derivatized carbon nanotubes, then
 reacting fluorine derivatized carbon nanotubes with a
 nucleophile. Some of the fluorine substituents are replaced
 by nucleophilic substitution. If desired, the remaining fluo-
 rine can be completely or partially eliminated to produce
 single wall carbon nanotubes having substituents attached to
 the side wall of the nanotube. The substituents will, of
 course, be dependent on the nucleophile, and preferred
 nucleophiles include alkyl lithium species such as methyl
 lithium. Alternatively, fluorine may be fully or partially
 removed from fluorine derivatized carbon nanotubes by
 reacting the fluorine derivatized carbon nanotubes with
 various amounts of hydrazine, substituted hydrazine or alkyl
 amine. The present invention also provides seed materials
 for growth of single wall carbon nanotubes comprising a
 plurality of single wall carbon nanotubes or short tubular
 molecules having a catalyst precursor moiety covalently
 bound or physisorbed on the outer surface of the sidewall to
 provide the optimum metal cluster size under conditions that
 result in migration of the metal moiety to the tube end.

54 Claims, 26 Drawing Sheets

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FIG. 1A

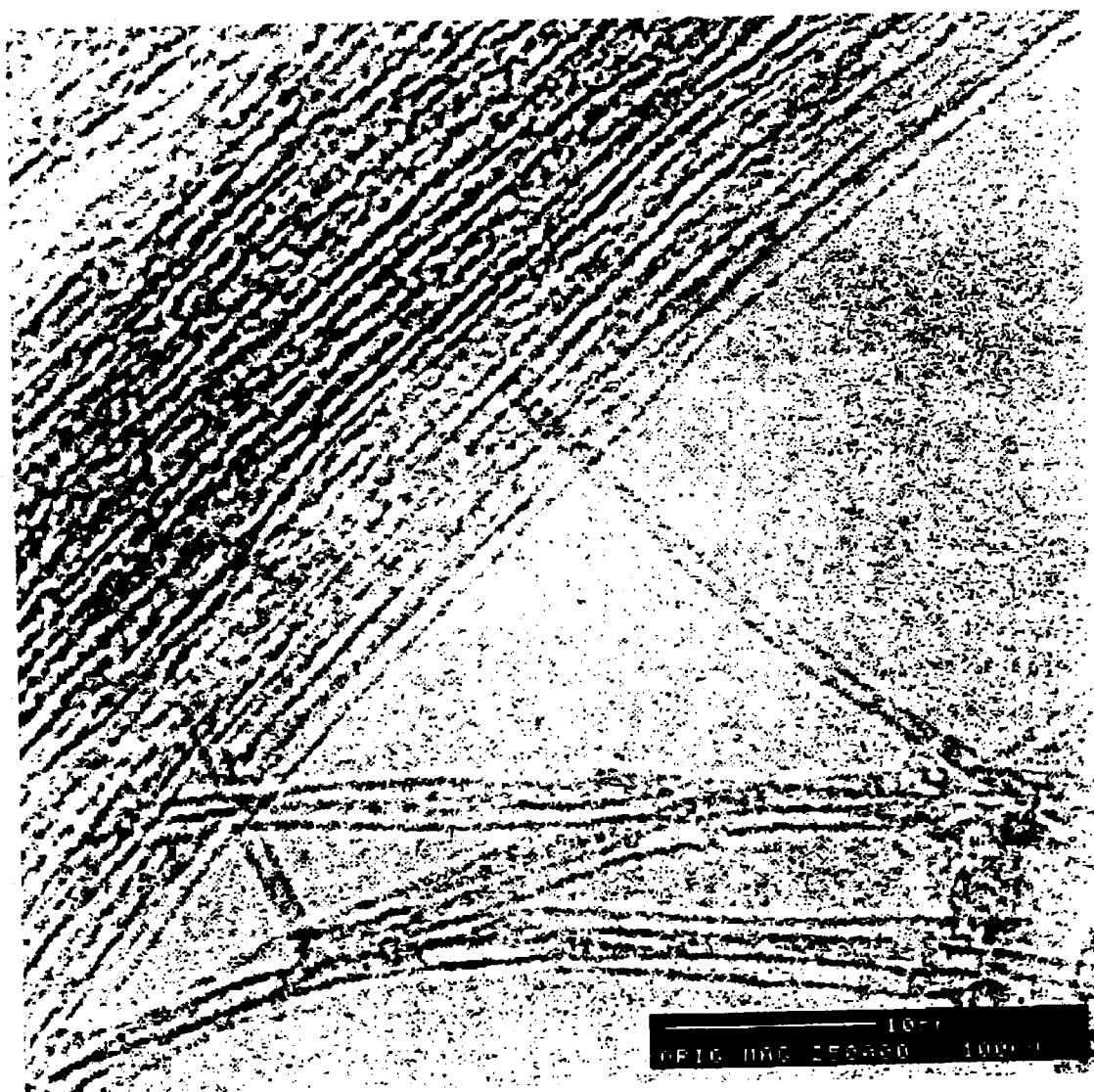


FIG. 1B

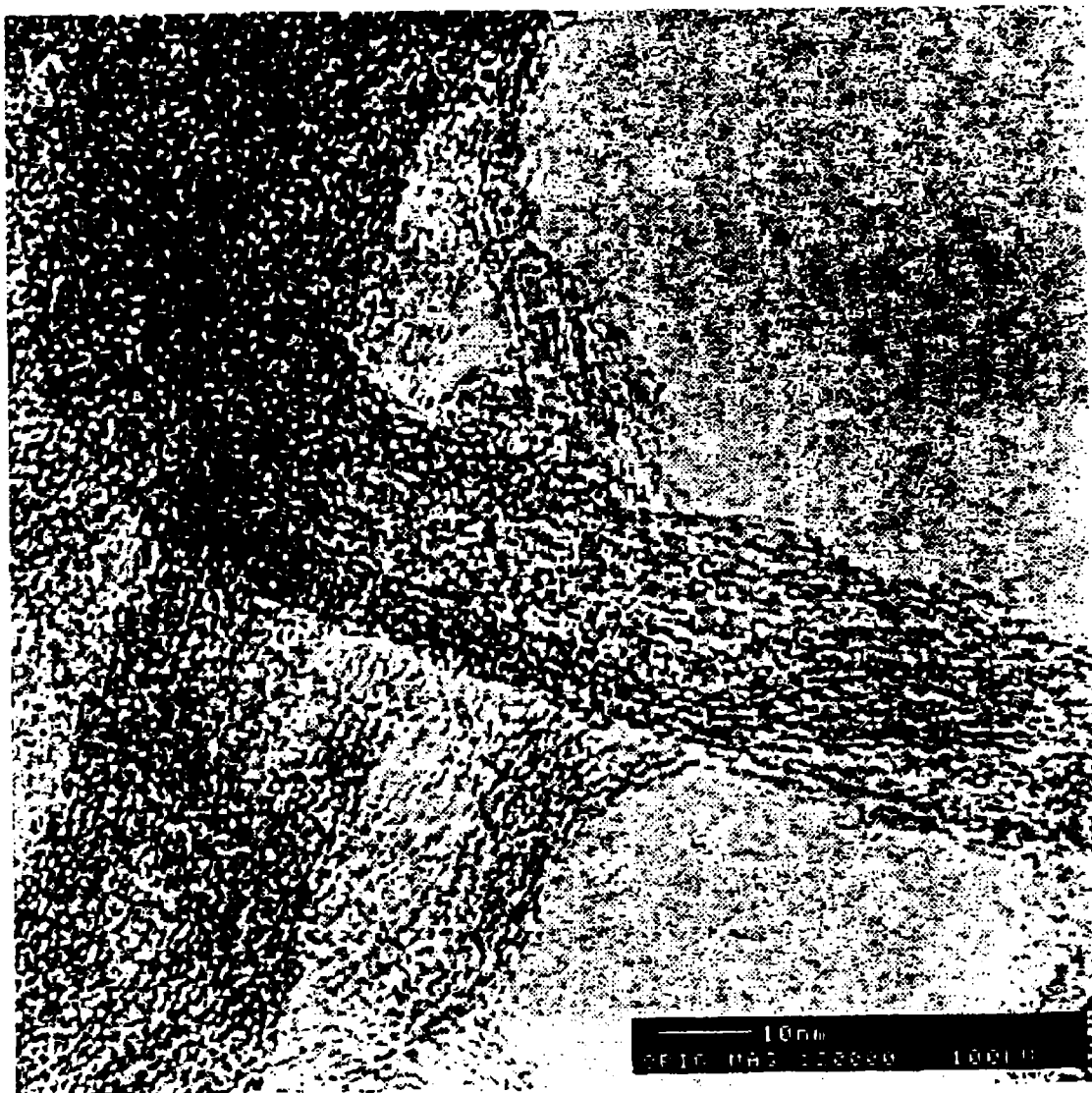


FIG. 1C



FIG. 1D

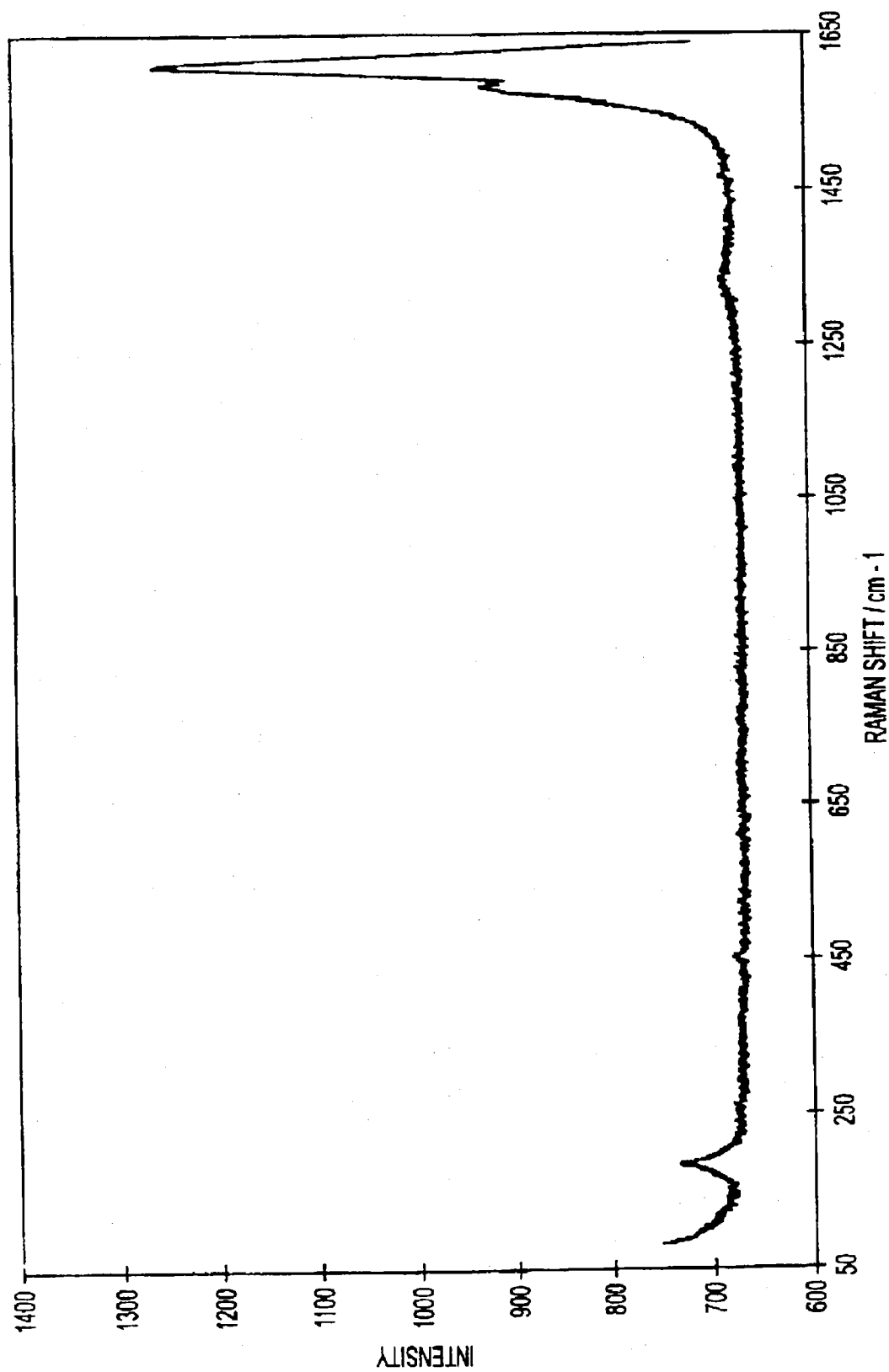


FIG. 2

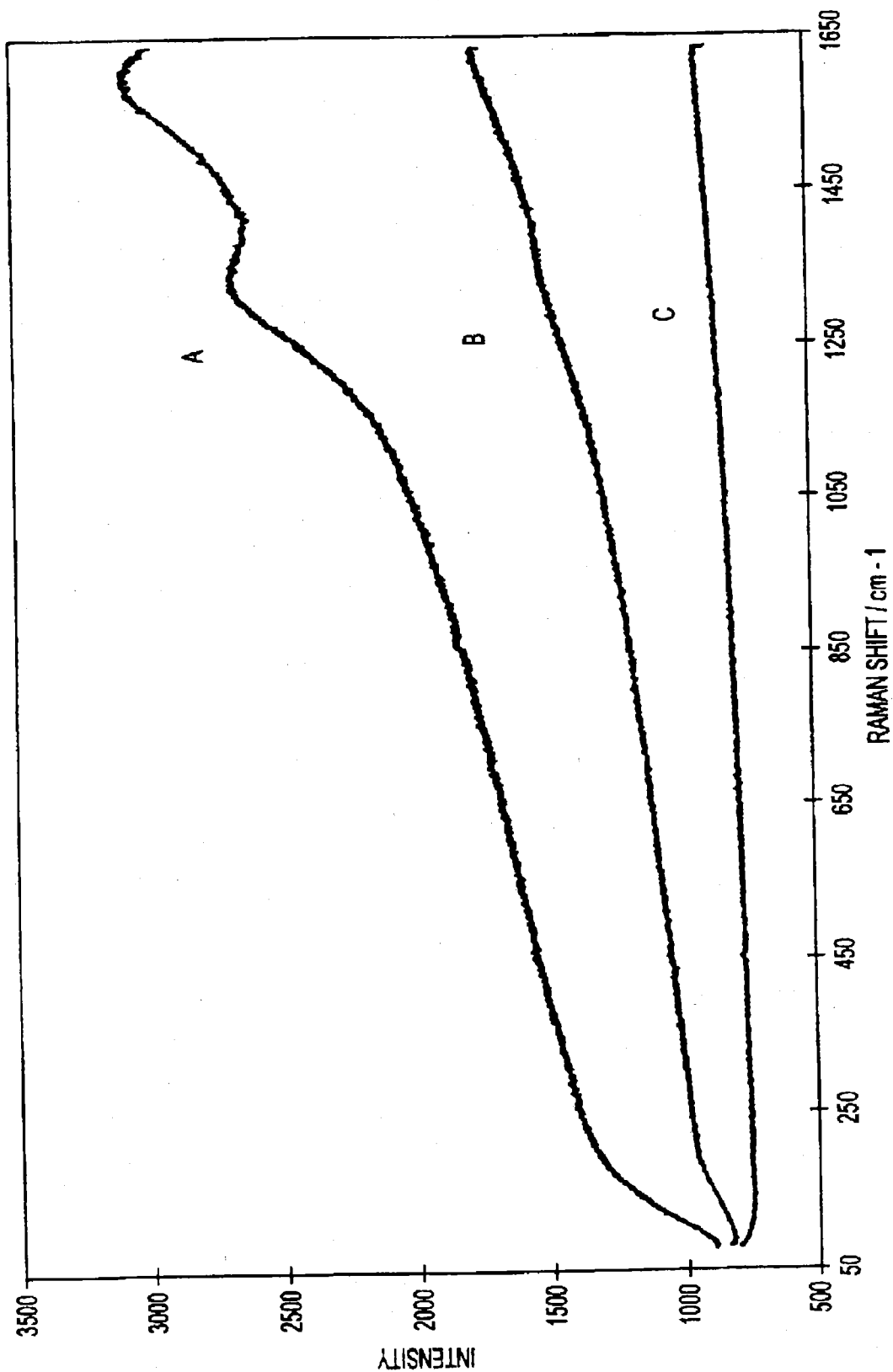


FIG. 3

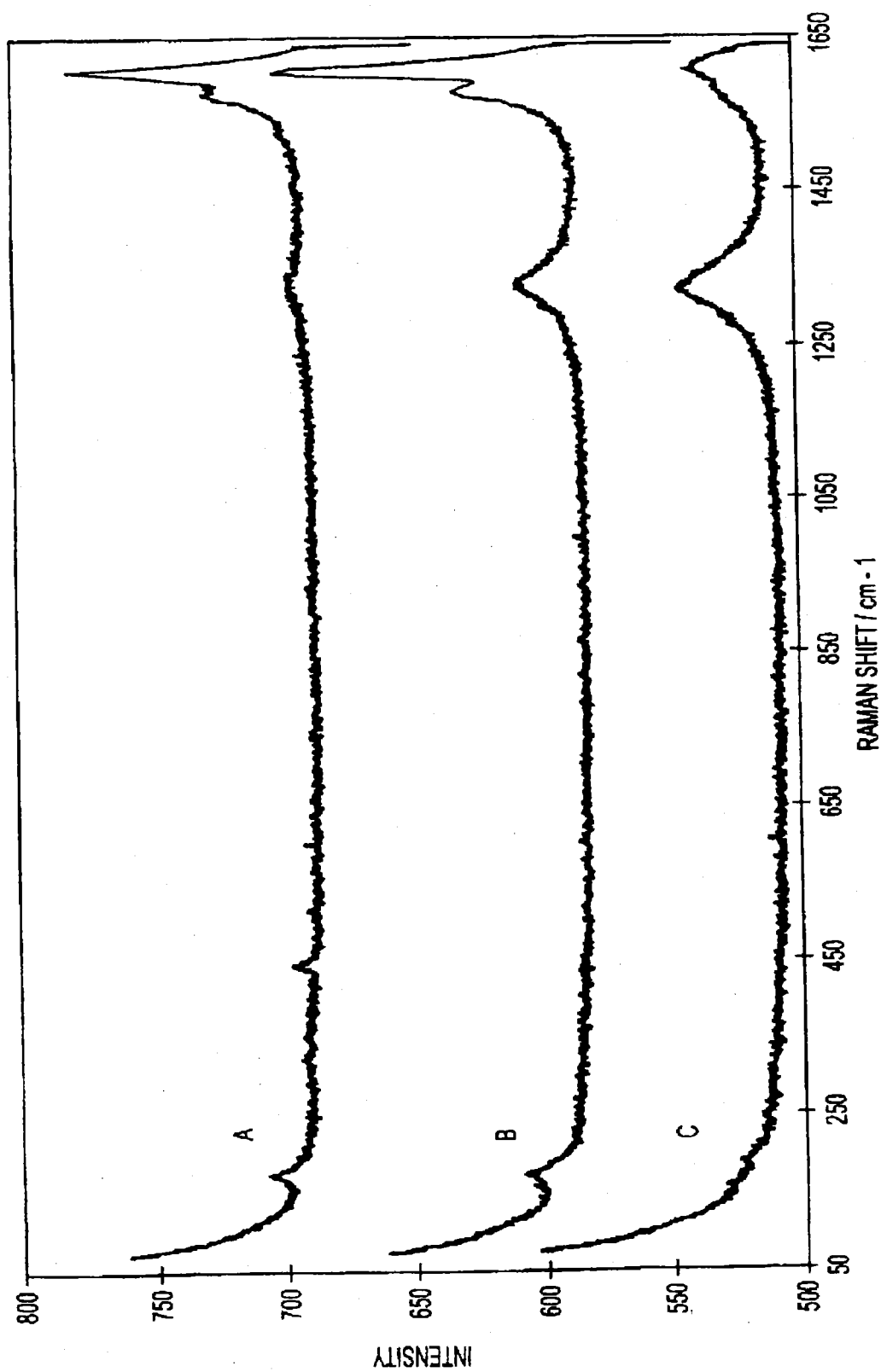


FIG. 4

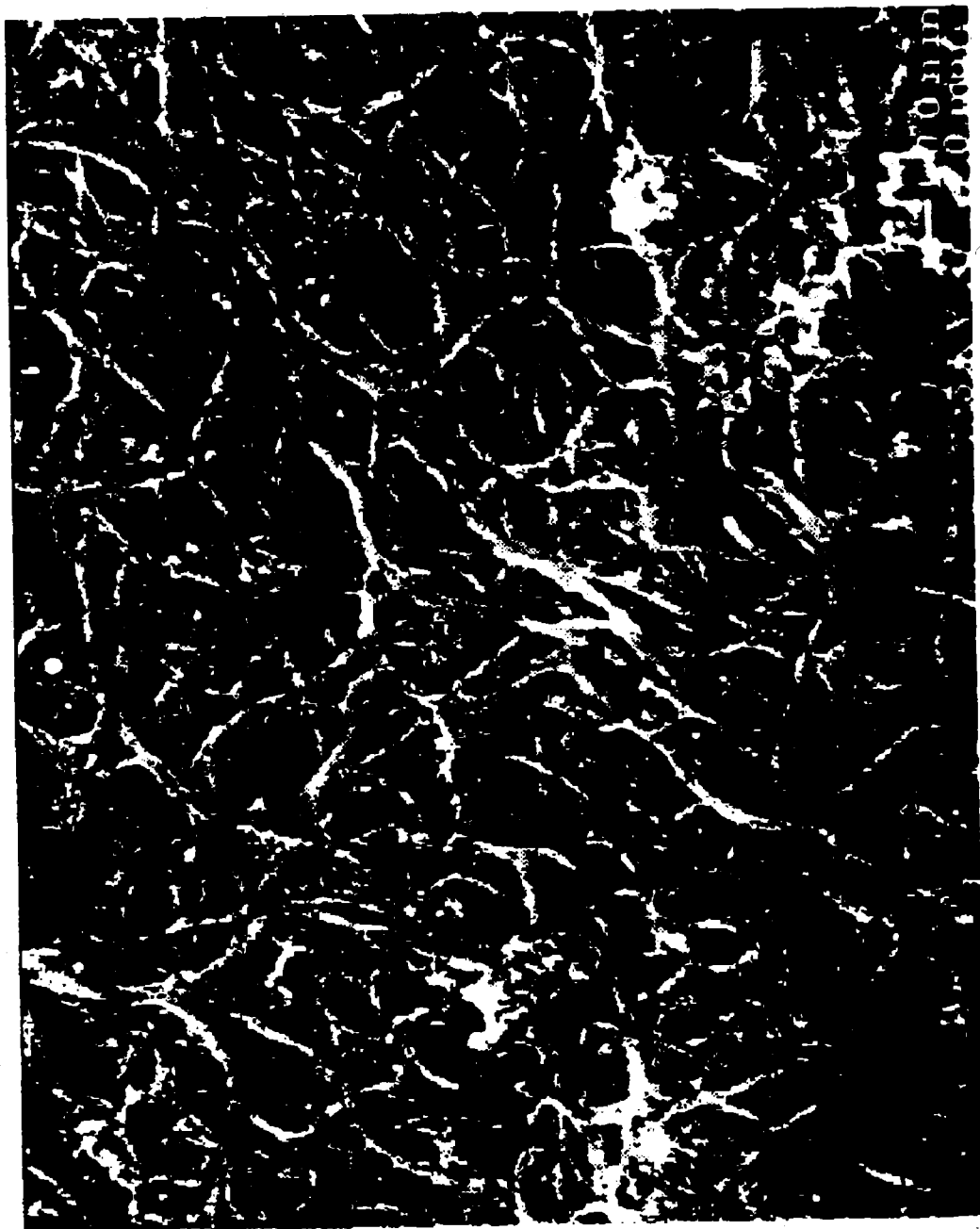


FIG. 5A

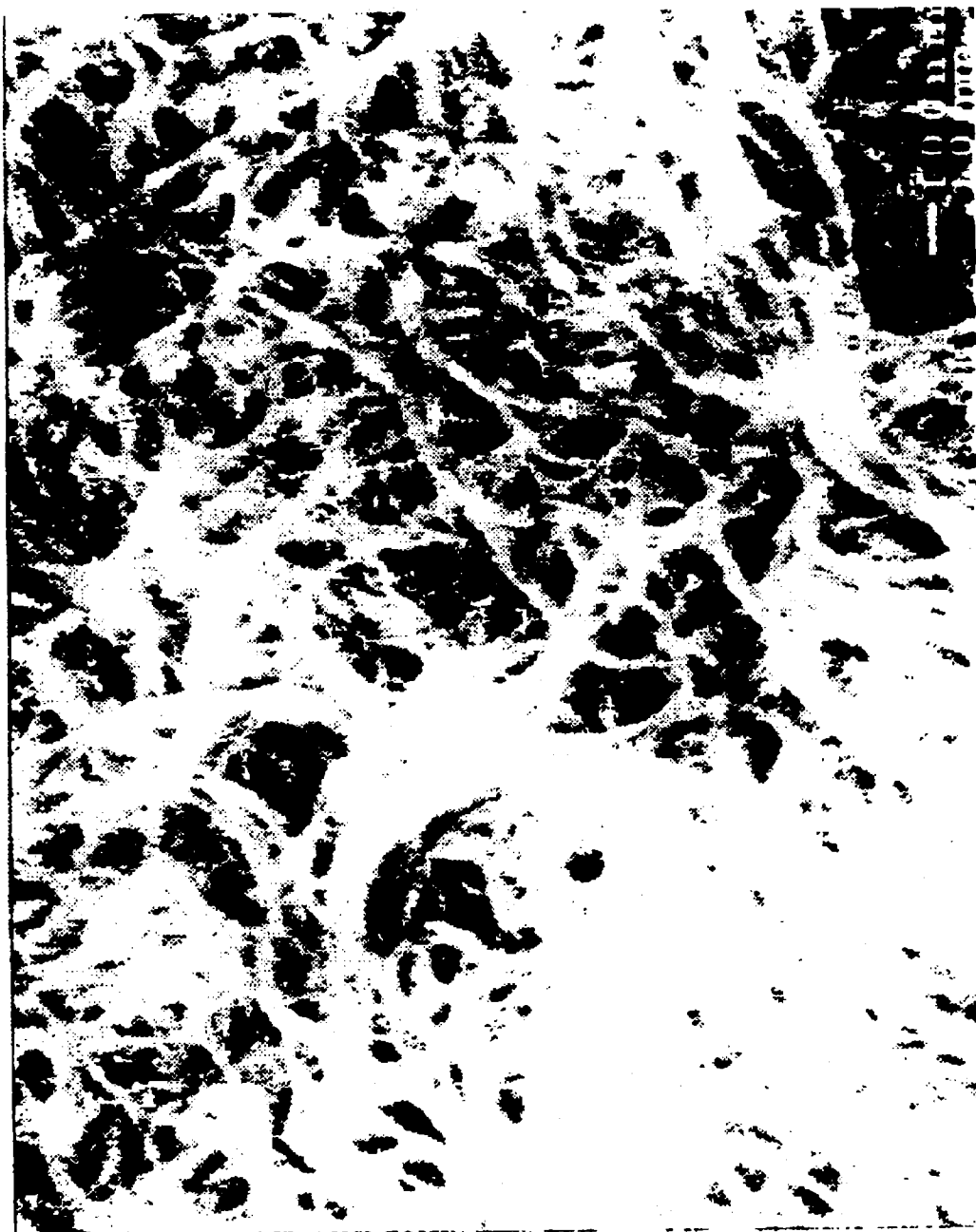


FIG. 5B



FIG. 5C

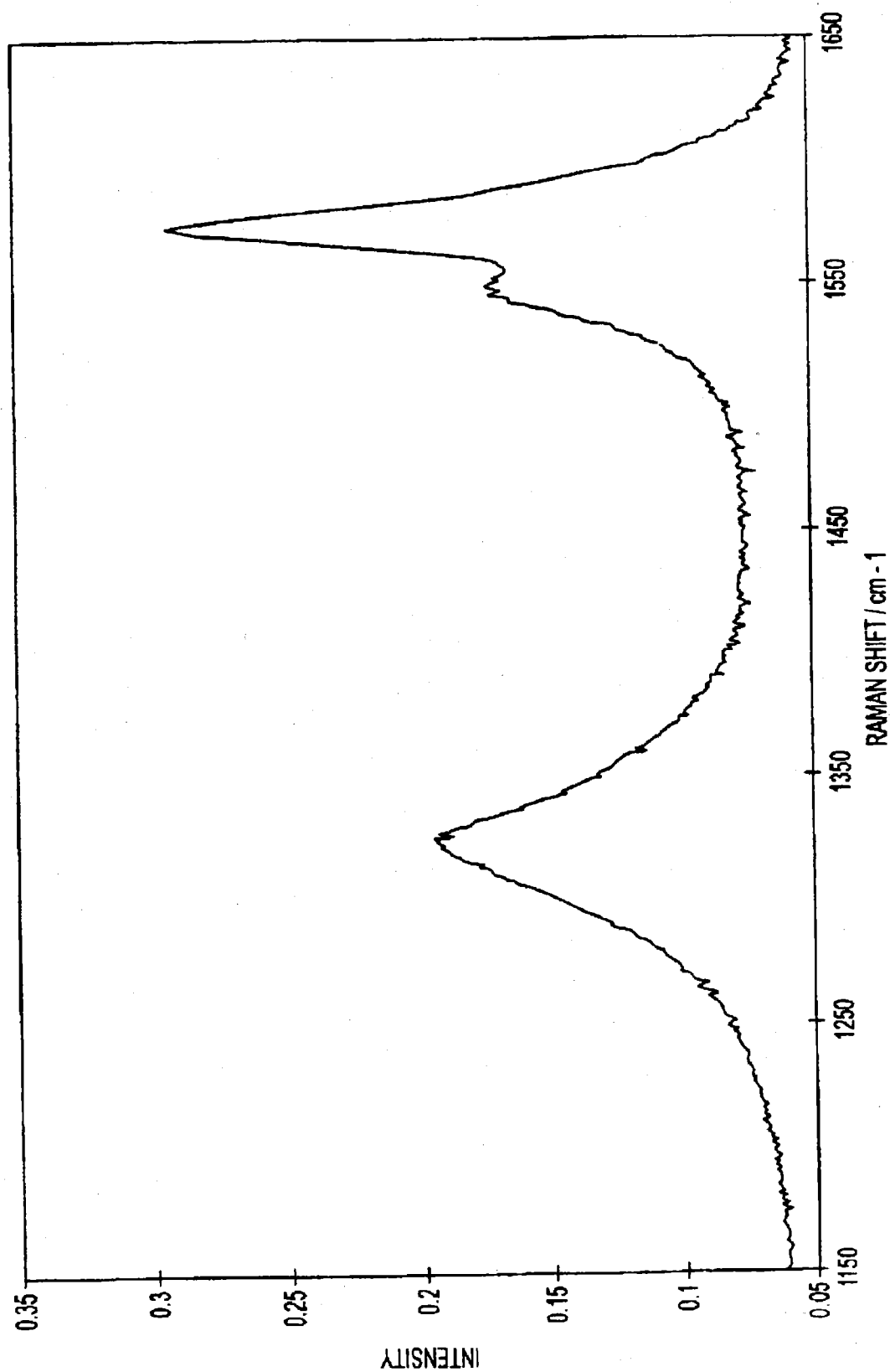


FIG. 6A

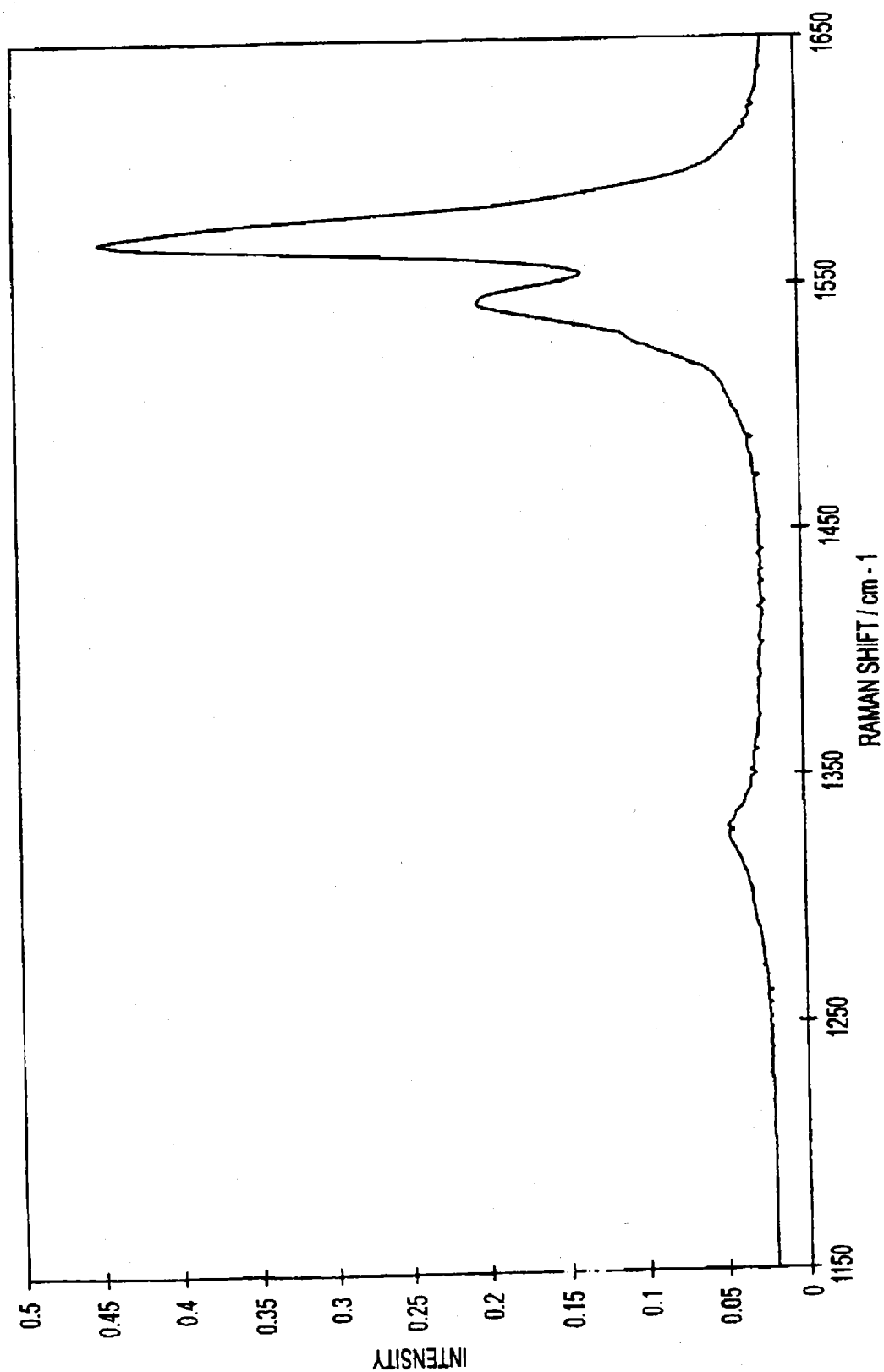


FIG. 6B

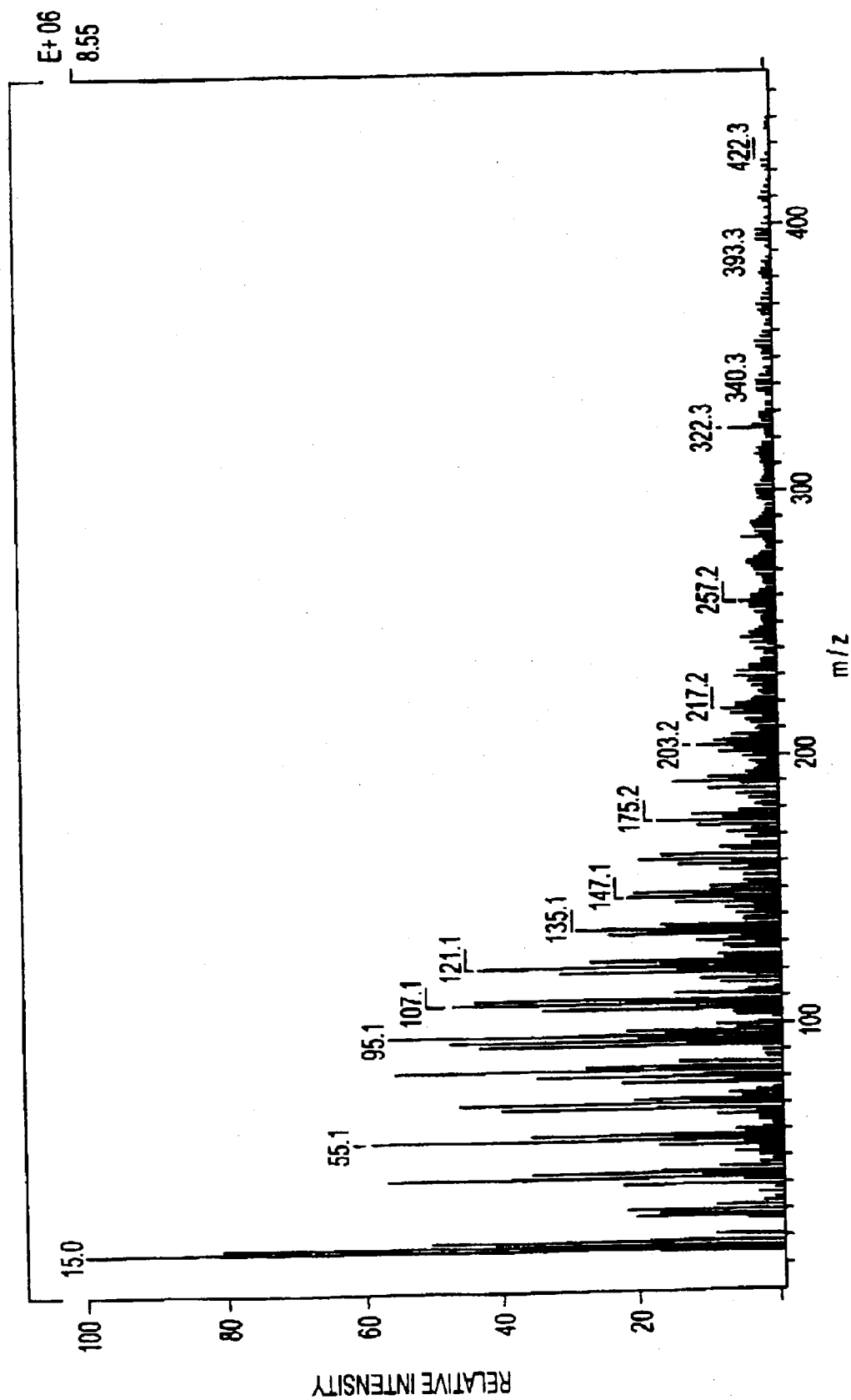


FIG. 7

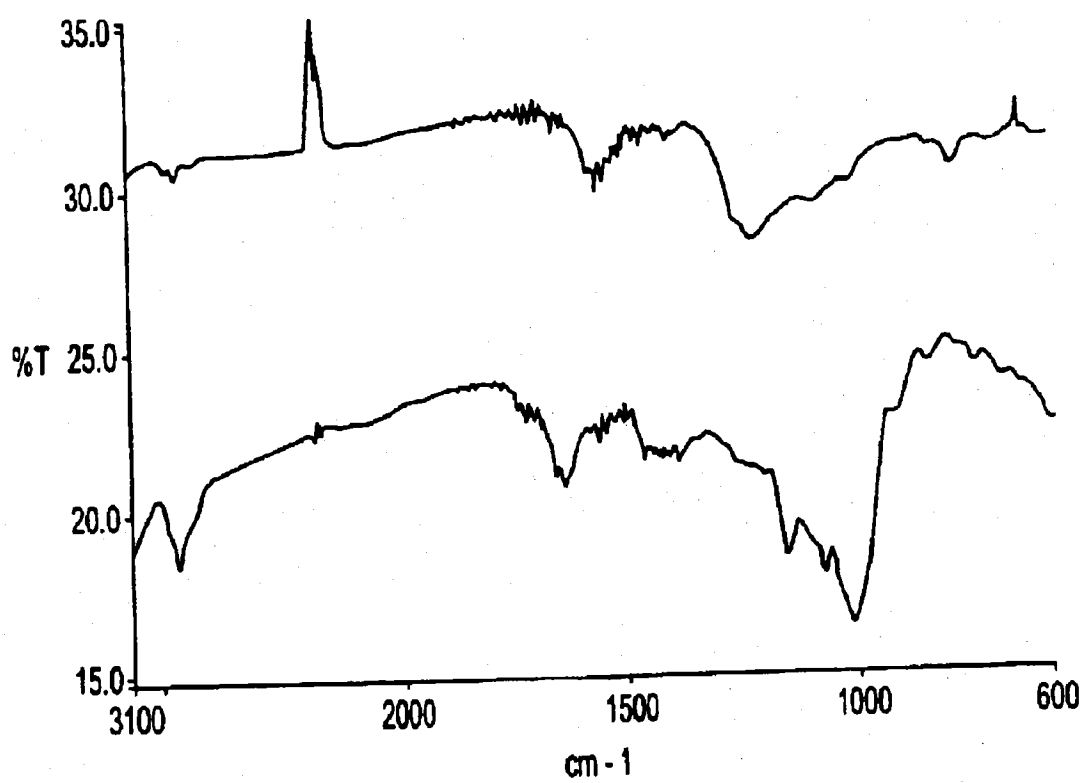


FIG. 8

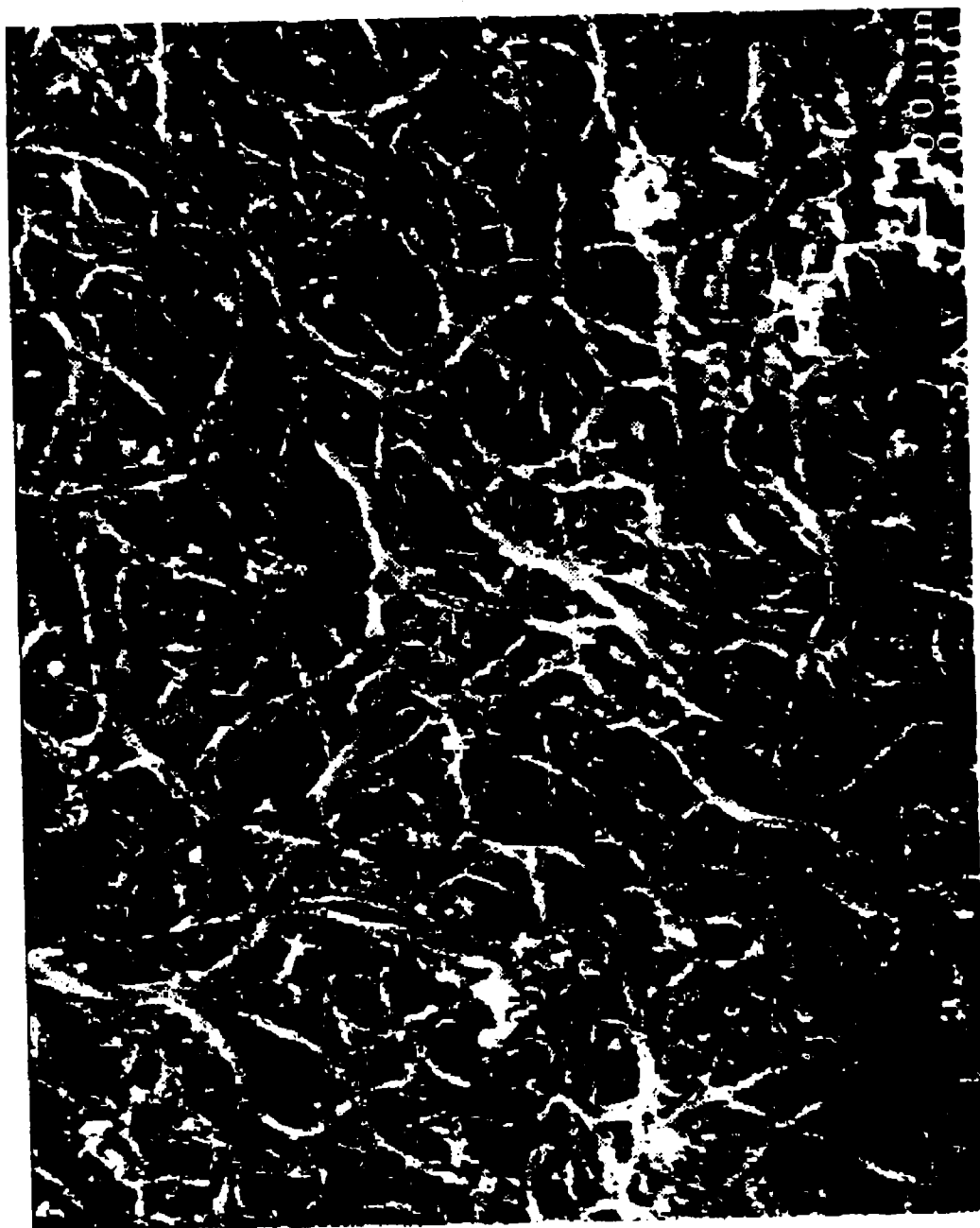


FIG. 9

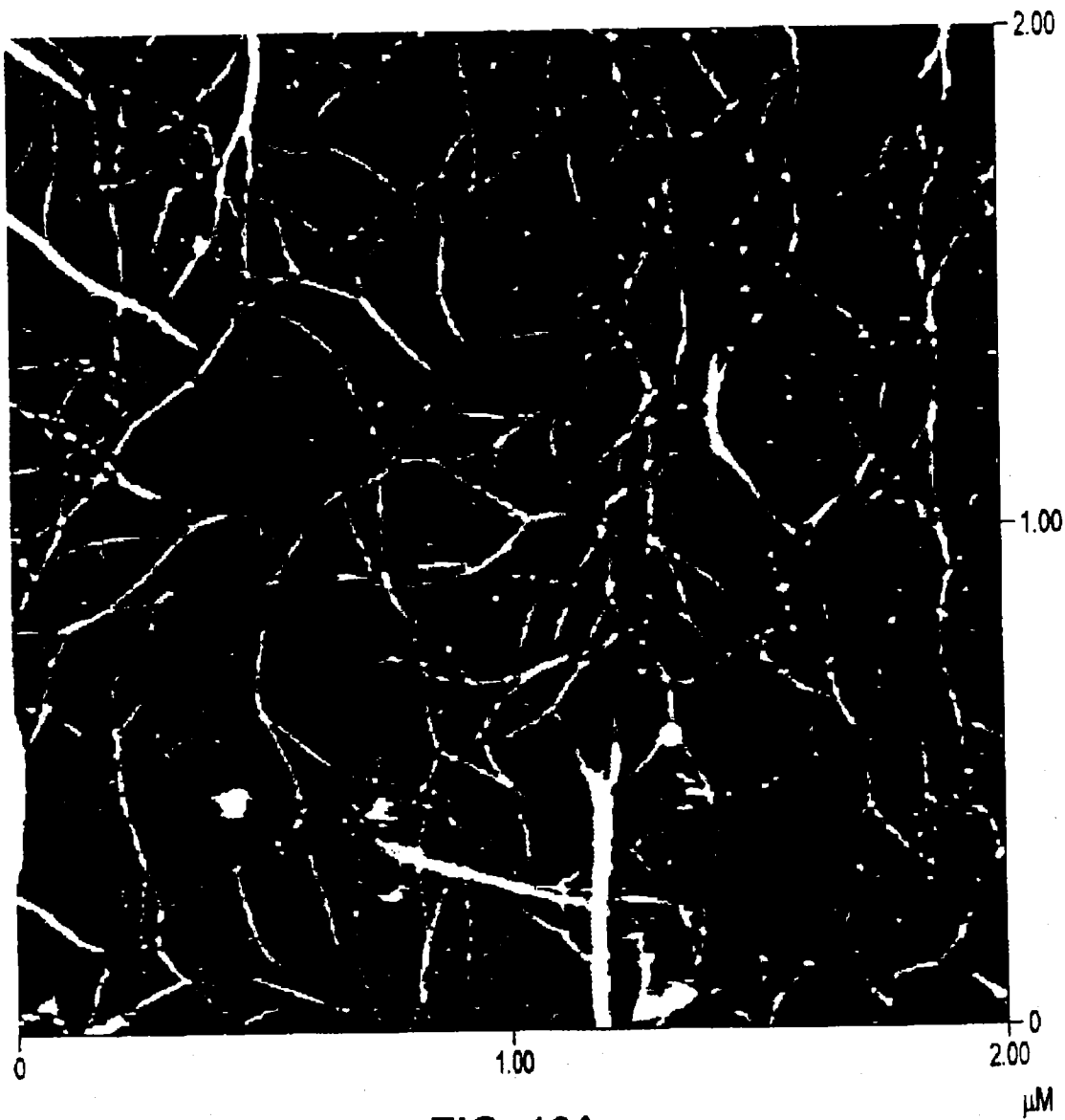


FIG. 10A

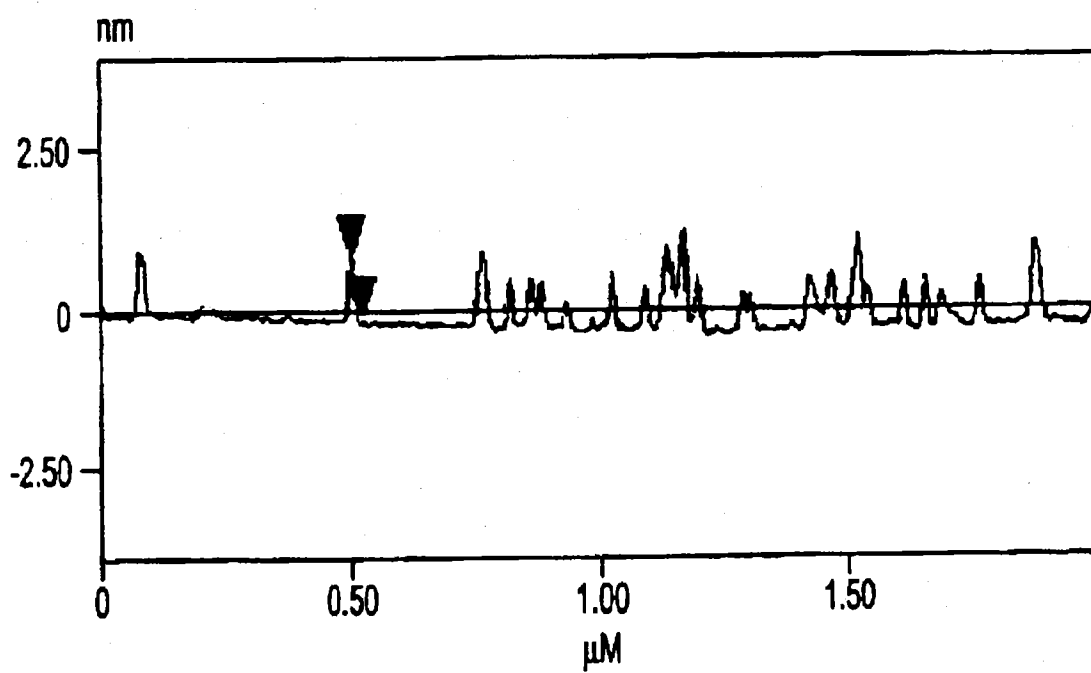


FIG. 10B

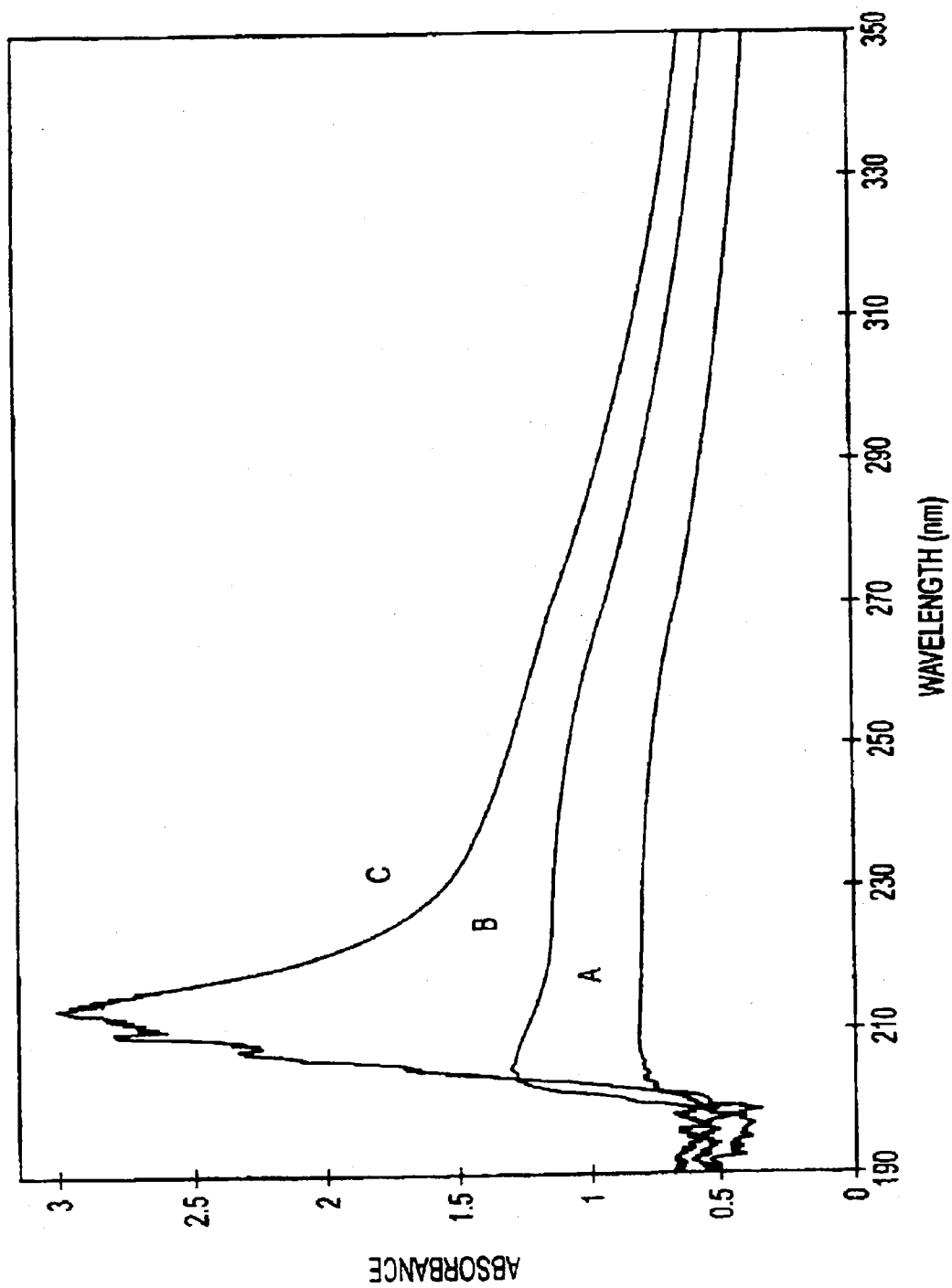


FIG. 11

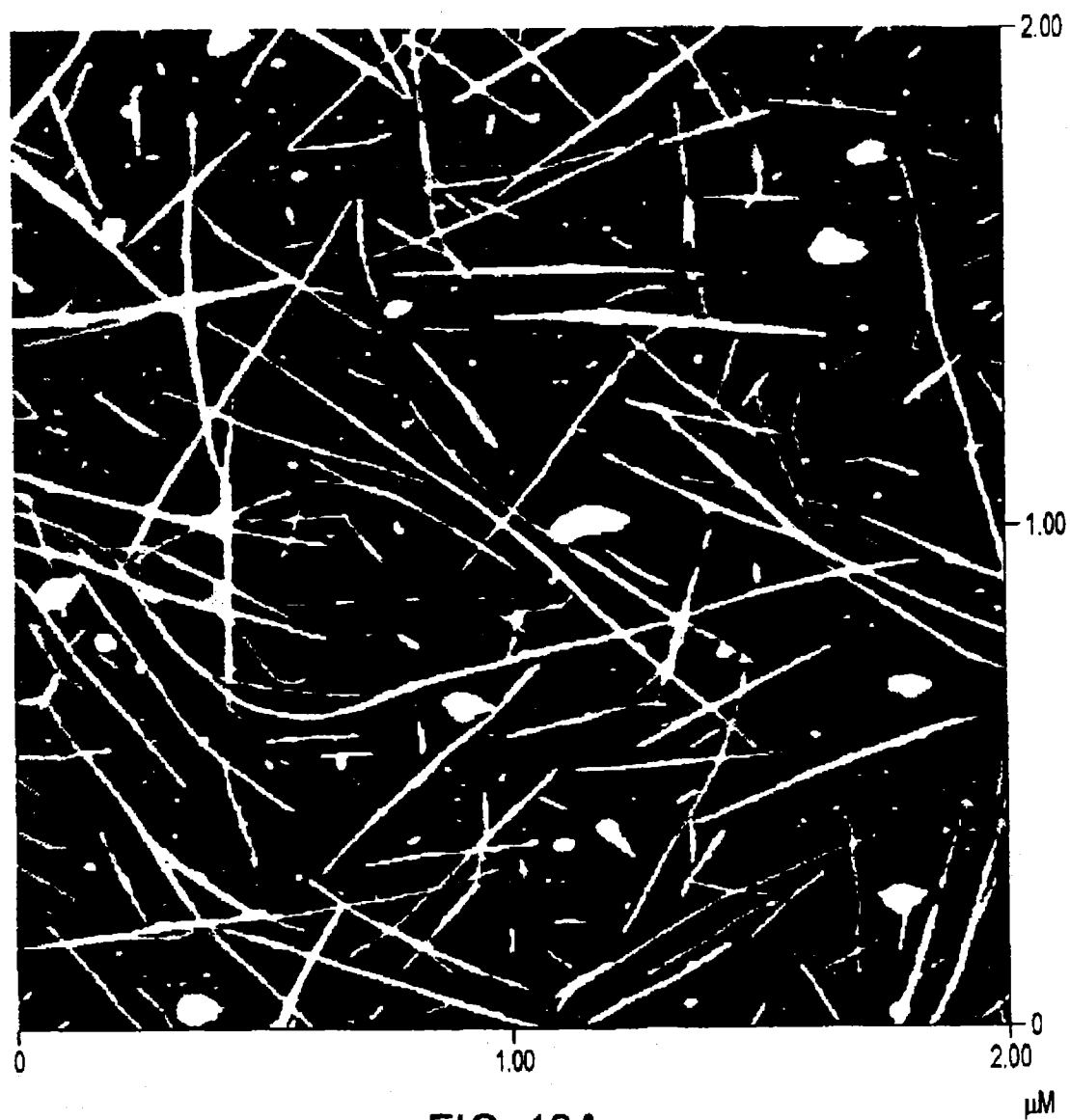


FIG. 12A

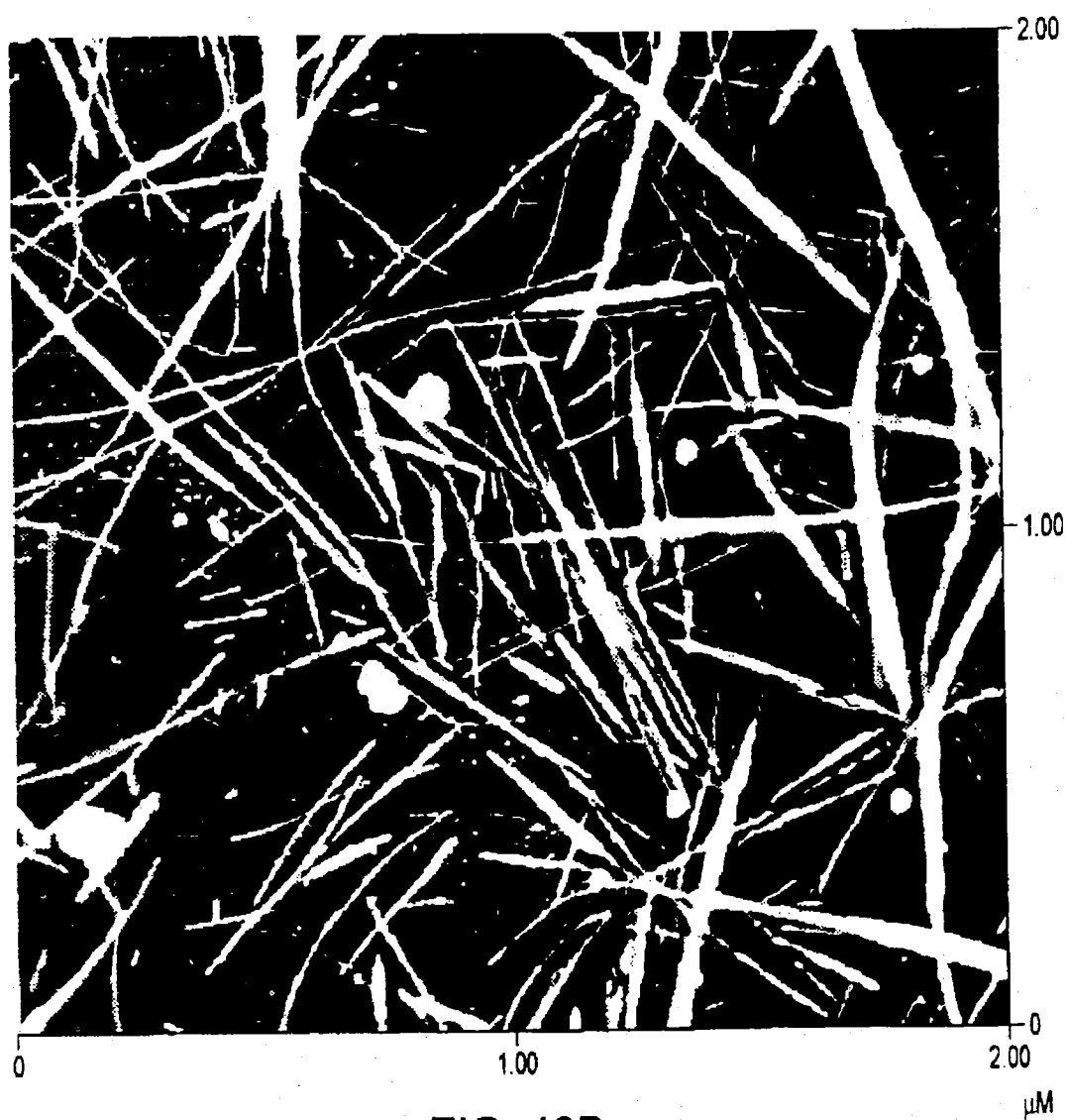


FIG. 12B

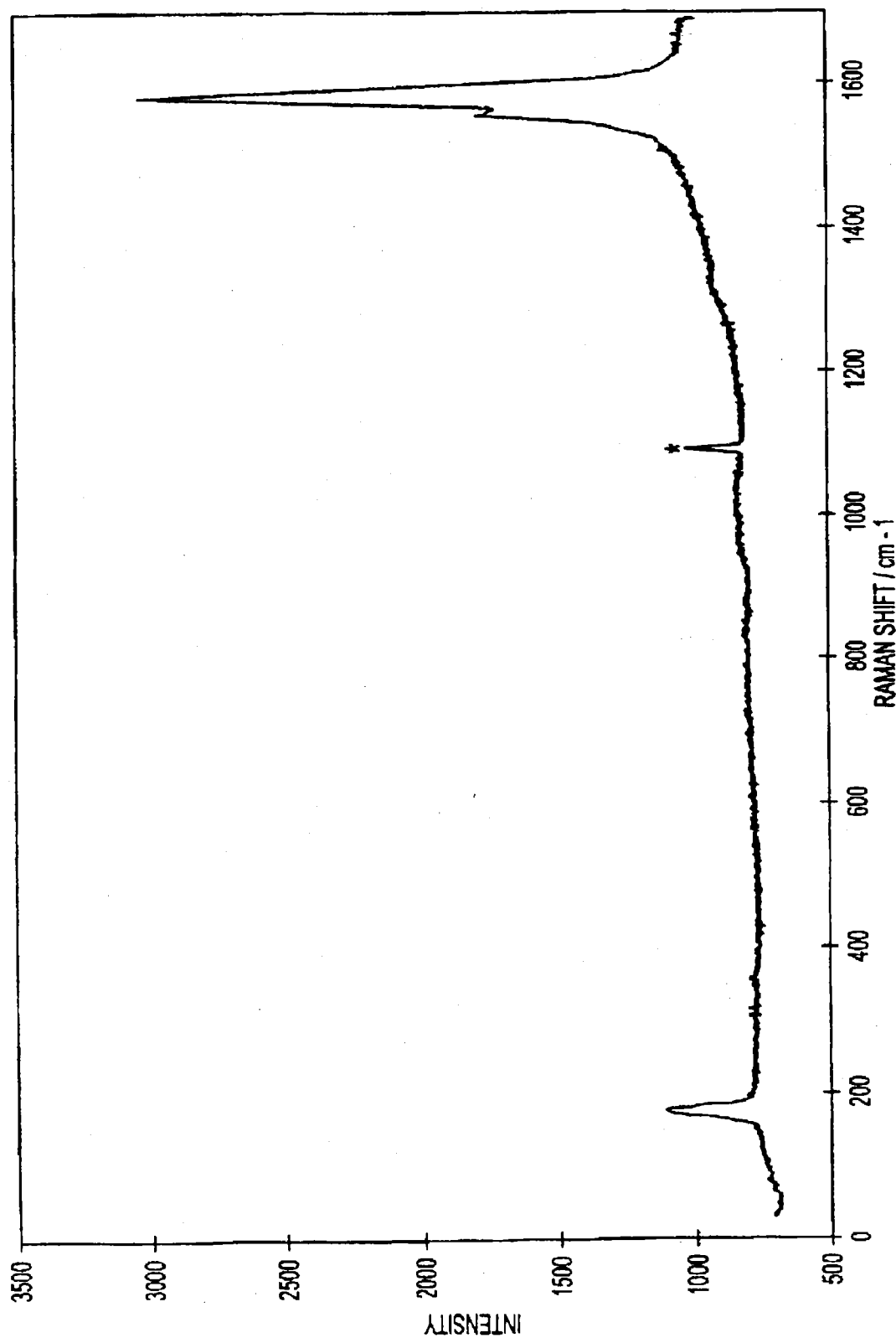
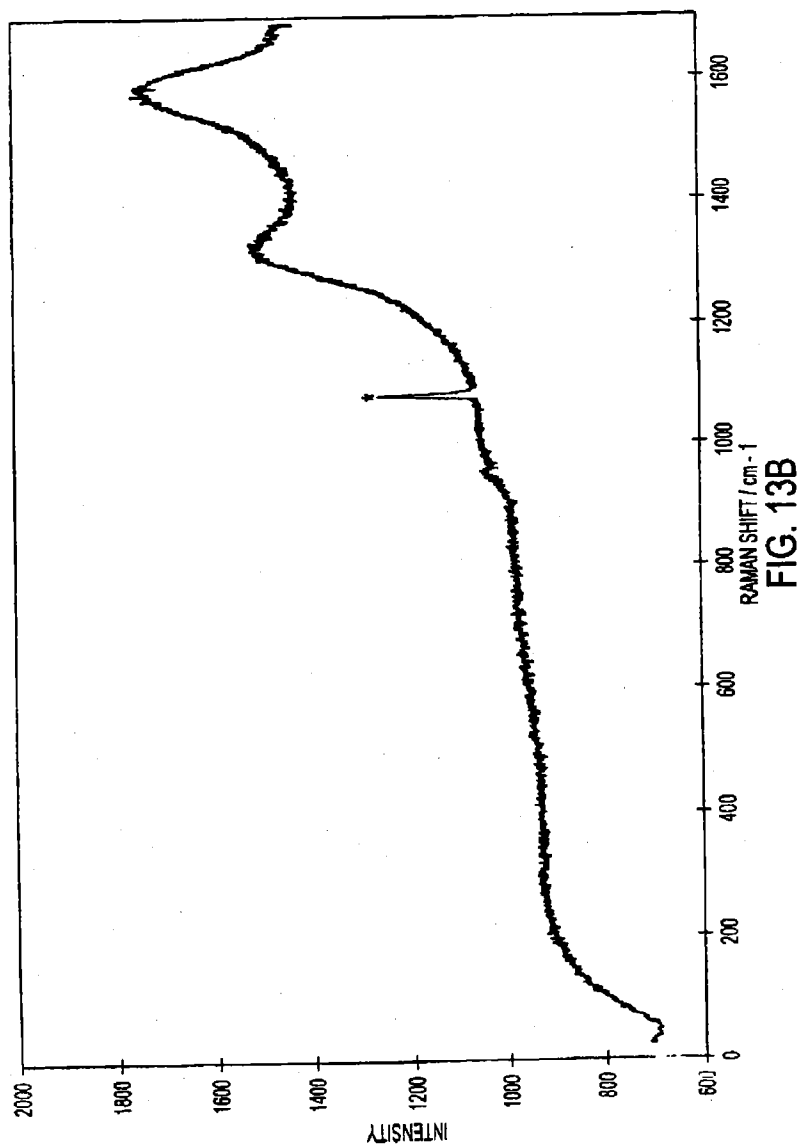


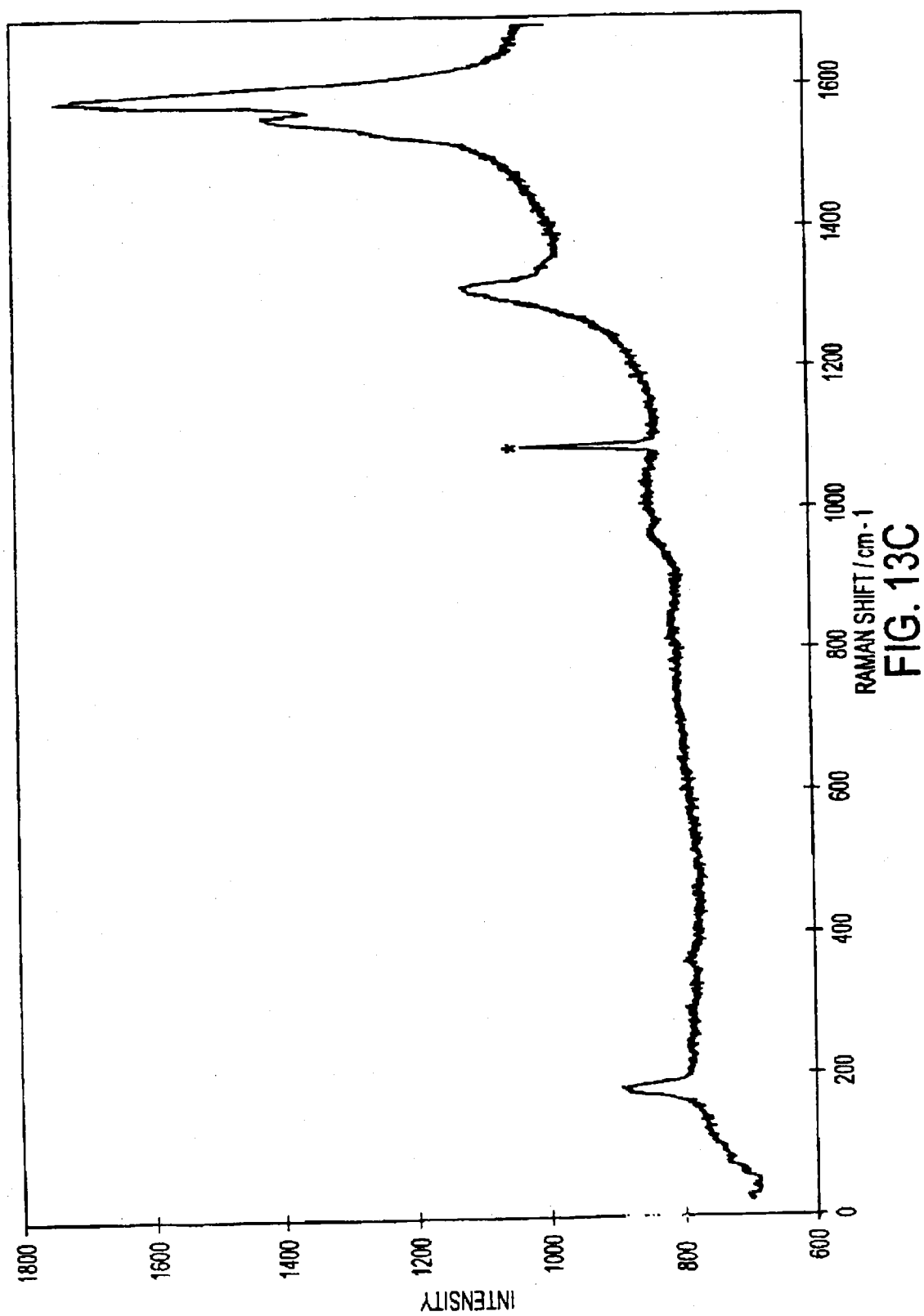
FIG. 13A

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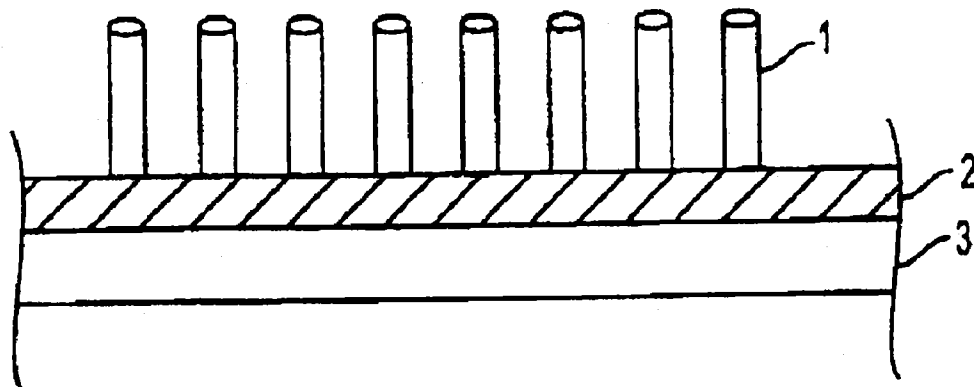


FIG. 14

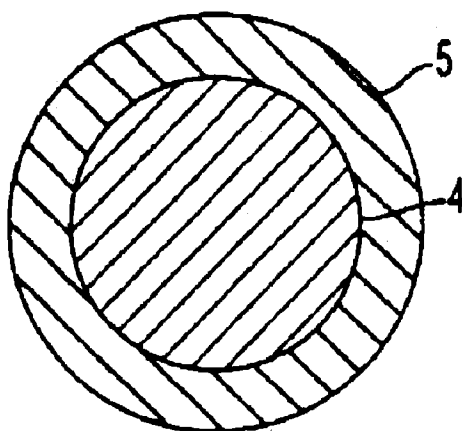


FIG. 15

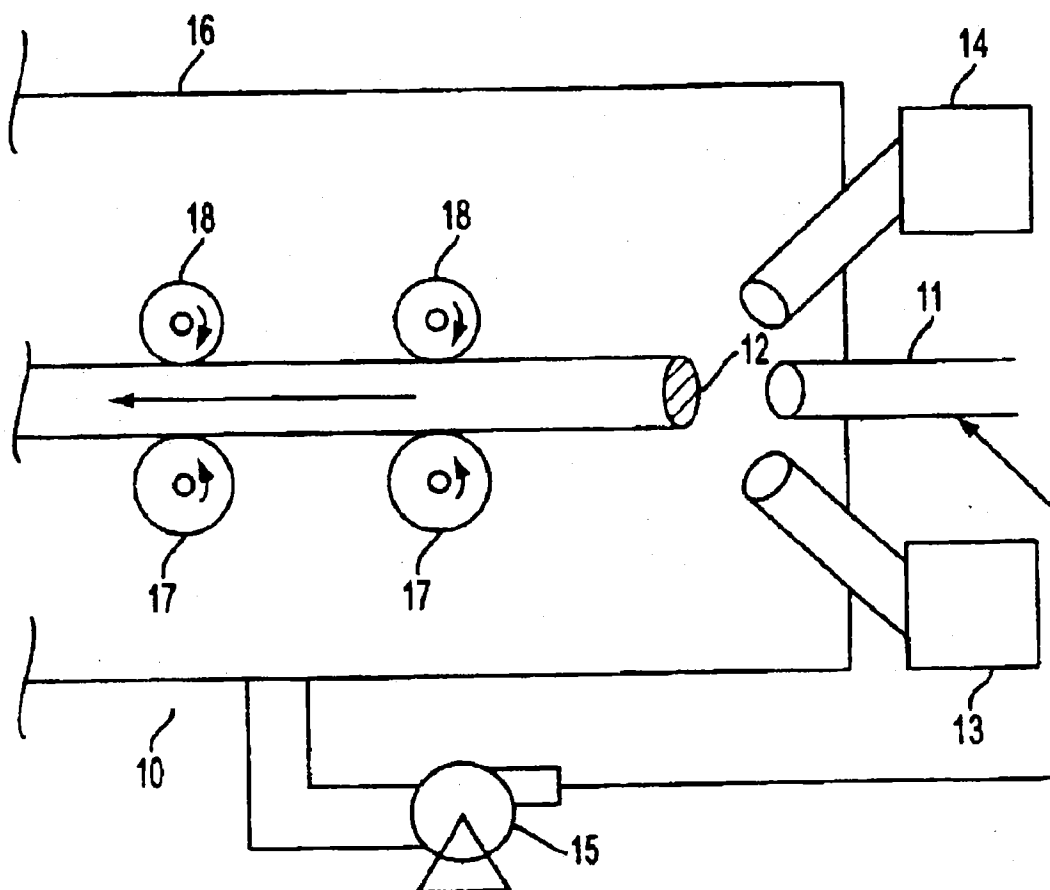


FIG. 16

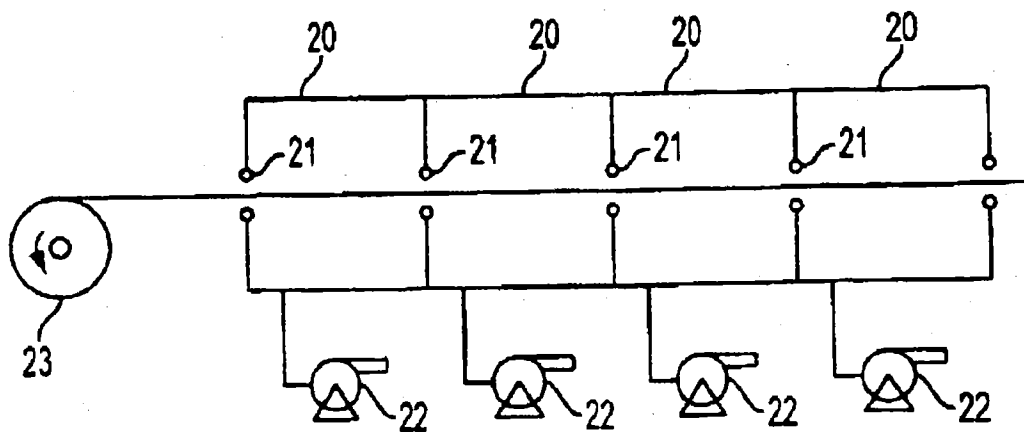


FIG. 17

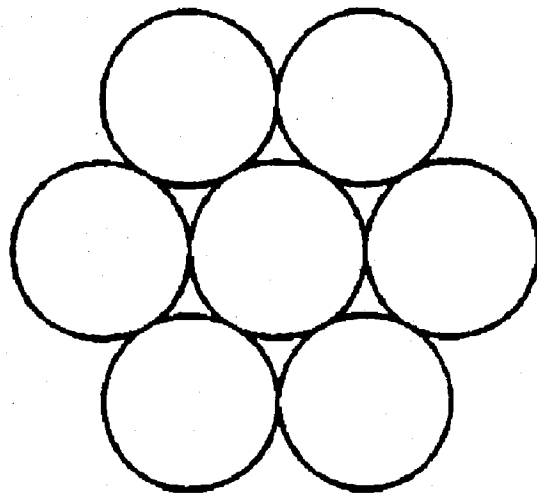


FIG. 18

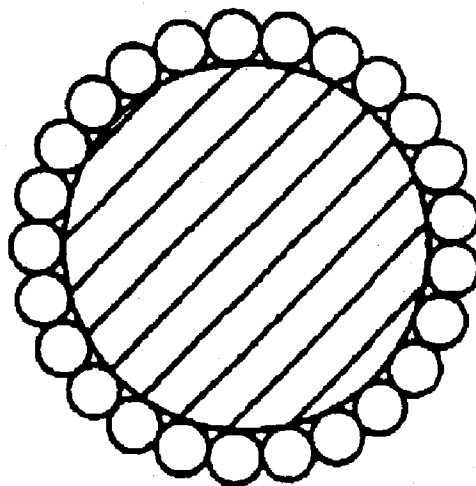


FIG. 19

DISPERSIONS AND SOLUTIONS OF FLUORINATED SINGLE-WALL CARBON NANOTUBES

PRIORITY BENEFIT AND CROSS REFERENCE TO RELATED APPLICATIONS

This Application is a divisional application U.S. patent application Ser. No. 09/787,473 filed on Mar. 16, 2001, "CHEMICAL DERIVATIZATION OF SINGLE-WALL CARBON NANOTUBES TO FACILITATE SOLVATION THEREOF; AND USE OF DERIVATIZED NANOTUBES TO FORM CATALYST-CONTAINING SEED MATERIALS FOR USE IN MAKING CARBON FIBERS" to Margraves et al., filed concurrent to the date of this Application. This application claims priority benefits to U.S. patent application Ser. No. 09/787,473, and claims priority benefits to International Application No. PCT/US99/21366, filed Sep. 17, 1999, which application claims priority benefits to U.S. patent application Ser. Nos. (1) 60/101,092, filed Sep. 18, 1998; (2) 60/106,918 filed Nov. 3, 1998; and (3) 60/138,505, filed Jun. 10, 1999, all of which are hereby incorporated by reference.

The present invention is related to the following corresponding U.S. Patent Applications, all of which are divisionals of the U.S. patent application Ser. No. 09/787,473:

U.S. patent application Ser. No. 09/810,390, "CHEMICAL DERIVATIZATION OF SINGLE-WALL CARBON NANOTUBES TO FACILITATE SOLVATION THEREOF; AND USE OF DERIVATIZED NANOTUBES TO FORM CATALYST-CONTAINING SEED MATERIALS FOR USE IN MAKING CARBON FIBERS" to Margraves et al., filed concurrent to the date of this Application;

U.S. patent application Ser. No. 09/809,885, "CHEMICAL DERIVATIZATION OF SINGLE-WALL CARBON NANOTUBES TO FACILITATE SOLVATION THEREOF; AND USE OF DERIVATIZED NANOTUBES TO FORM CATALYST-CONTAINING SEED MATERIALS FOR USE IN MAKING CARBON FIBERS" to Margraves et al., filed concurrent to the date of this Application;

U.S. patent application Ser. No. 09/810,150, "CHEMICAL DERIVATIZATION OF SINGLE-WALL CARBON NANOTUBES TO FACILITATE SOLVATION THEREOF; AND USE OF DERIVATIZED NANOTUBES TO FORM CATALYST-CONTAINING SEED MATERIALS FOR USE IN MAKING CARBON FIBERS" to Margraves et al., filed concurrent to the date of this Application;

U.S. patent application Ser. No. 09/810,201, "CHEMICAL DERIVATIZATION OF SINGLE-WALL CARBON NANOTUBES TO FACILITATE SOLVATION THEREOF; AND USE OF DERIVATIZED NANOTUBES TO FORM CATALYST-CONTAINING SEED MATERIALS FOR USE IN MAKING CARBON FIBERS" to Margraves et al., filed concurrent to the date of this Application;

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is directed to making chemical derivatives of carbon nanotubes and to uses for the derivatized nanotubes, including making arrays as a basis for synthesis of carbon fibers.

2. Related Art

Fullerenes are closed-cage molecules composed entirely of sp^2 -hybridized carbons, arranged in hexagons and pentagons. Fullerenes (e.g., C_{60}) were first identified as closed spheroidal cages produced by condensation from vaporized carbon.

Fullerene tubes are produced in carbon deposits on the cathode in carbon arc methods of producing spheroidal fullerenes from vaporized carbon. Ebbesen et al. (Ebbesen I) "Large-Scale Synthesis Of Carbon Nanotubes," *Nature*, Vol. 358, p. 220 (Jul. 16, 1992) and Ebbesen et al., (Ebbesen II), "Carbon Nanotubes," *Annual Review of Materials Science*, Vol. 24, p. 235 (1994). Such tubes are referred to herein as carbon nanotubes. Many of the carbon nanotubes made by these processes were multi-wall nanotubes, i.e., the carbon nanotubes resembled concentric cylinders. Carbon nanotubes having up to seven walls have been described in the prior art. Ebbesen II; Iijima et al., "Helical Microtubes Of Graphitic Carbon," *Nature*, Vol. 354, p. 56 (Nov. 7, 1991). Production of Single-wall Nanotubes

Single-wall carbon nanotubes (SWNT) have been made in a DC arc discharge apparatus of the type used in fullerene production by simultaneously evaporating carbon and a small percentage of VIII B transition metal from the anode of the arc discharge apparatus. See Iijima et al., "Single-Shell Carbon Nanotubes of 1 nm Diameter," *Nature*, Vol. 363, p. 603 (1993); Bethune et al., "Cobalt Catalyzed Growth of Carbon Nanotubes with Single Atomic Layer Walls," *Nature*, Vol. 63, p. 605 (1993); Ajayan et al., "Growth Morphologies During Cobalt Catalyzed Single-Shell Carbon Nanotube Synthesis," *Chem. Phys. Lett.*, Vol. 215, p. 509 (1993); Zhou et al., "Single-Walled Carbon Nanotubes Growing Radially From YC_2 Particles," *Appl. Phys. Lett.*, Vol. 65, p. 1593 (1994); Seraphin et al., "Single-Walled Tubes and Encapsulation of Nanocrystals Into Carbon Clusters," *Electrochem. Soc.*, Vol. 142, p. 290 (1995); Saito et al., "Carbon Nanocapsules Encaging Metals and Carbides," *J. Phys. Chem. Solids*, Vol. 54, p. 1849 (1993); Saito et al., "Extrusion of Single-Wall Carbon Nanotubes Via Formation of Small Particles Condensed Near an Evaporation Source," *Chem. Phys. Lett.*, Vol. 236, p. 419 (1995). It is also known that the use of mixtures of such transition metals can significantly enhance the yield of single-wall carbon nanotubes in the arc discharge apparatus. See Lambert et al., "Improving Conditions Toward Isolating Single-Shell Carbon Nanotubes," *Chem. Phys. Lett.*, Vol. 226, p. 364 (1994). While the arc discharge process can produce single-wall nanotubes, the yield of nanotubes is low and the tubes exhibit significant variations in structure and size between individual tubes in the mixture. Individual carbon nanotubes are difficult to separate from the other reaction products and purify.

An improved method of producing single-wall nanotubes is described in U.S. Ser. No. 08/687,665, entitled "Ropes of Single-Walled Carbon Nanotubes" incorporated herein by reference in its entirety. This method uses, inter alia, laser vaporization of a graphite substrate doped with transition metal atoms, preferably nickel, cobalt, or a mixture thereof, to produce single-wall carbon nanotubes in yields of at least 50% of the condensed carbon. The single-wall nanotubes produced by this method tend to be formed in clusters, termed "ropes," of 10 to 1000 single-wall carbon nanotubes in parallel alignment, held together by van der Waals forces in a closely packed triangular lattice. Nanotubes produced by this method vary in structure, although one structure tends to predominate.

A method of producing carbon fibers from single-wall carbon nanotubes is described in PCT Patent Application No. PCT/US98/04513, incorporated herein by reference in its entirety. The carbon fibers are produced using SWNT molecules in a substantially two-dimensional array made up of single-walled nanotubes aggregated (e.g., by van der Waals forces) in substantially parallel orientation to form a

monolayer extending in directions substantially perpendicular to the orientation of the individual nanotubes. In this process the seed array tubes are opened at the top (free) end and a catalyst cluster is deposited at this free end. A gaseous carbon source is then provided to grow the nanotube assembly into a fiber. In various processes involving metal cluster catalysis, it is important to provide the proper number of metal atoms to give the optimum size cluster for single wall nanotube formation.

Derivatization of Single-wall Nanotubes

Since the discovery of single wall carbon nanotubes (SWNTs) in 1993 (Iijima, S. and Ichihashi, T., *Nature* 1993,363:603-605), researchers have been searching for ways to manipulate them chemically. While there have been many reports and review articles on the production and physical properties of carbon nanotubes, reports on chemical manipulation of nanotubes have been slow to emerge. There have been reports of functionalizing nanotube ends with carboxylic groups (Rao, et al., *Chem. Commun.*, 1996, 1525-1526; Wong, et al., *Nature*, 1998,394:52-55), and then further manipulation to tether them to gold particles via thiol linkages (Liu, et al., *Science*, 1998, 280:1253-1256). Had-don and co-workers (Chen, et al., *Science*, 1998, 282:95-98) have reported solvating SWNTs by adding octadecylamine groups on the ends of the tubes and then adding dichloro-carbenes to the nanotube side wall, albeit in relatively low quantities (~2%). While theoretical results have suggested that functionalization of the nanotube side-wall is possible (Cahill, et al., *Tetrahedron*, 1996, 52 (14):5247-5256), experimental evidence confirming this theory has not been obtained.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a method for derivatizing carbon nanotubes, especially the side walls of single-wall carbon nanotubes.

It is another object of this invention to provide a high yield, single step method for producing large quantities of continuous macroscopic carbon fiber from single-wall carbon nanotubes using inexpensive carbon feedstocks at moderate temperatures.

It is yet another object of this invention to provide macroscopic carbon fiber made by such a method. These and other objects of this invention are met by one or more of the following embodiments.

This invention provides single wall carbon nanotubes and/or tubular carbon molecules derivatized with substituents covalently bonded to carbon atoms of the side wall of the nanotube or molecule. The substituents may in principle be attached on the interior and/or exterior of the nanotube side wall, but the attachment will not be predominantly on the exterior wall. In particular, the single wall carbon nanotubes may have substituents selected from fluorine, alkyl and phenyl attached to the side wall. Such single wall carbon nanotubes having fluorine covalently bonded to the side wall of the nanotube demonstrate high electrical resistance.

This invention also provides a method for derivatizing carbon nanotubes comprising reacting carbon nanotubes with fluorine gas, the fluorine gas preferably being free of F_2 . Where the carbon nanotubes are single wall nanotubes, and the temperature is at least 500° C., the product may be multiple wall carbon nanotubes derivatized with fluorine. Where the carbon nanotubes are single wall nanotubes, and the temperature is between 250° C. and 500° C., the product is single wall carbon nanotubes having fluorine covalently bonded to carbon atoms of the side wall of the nanotube.

In one embodiment, this invention also provides a method for preparing single wall carbon nanotubes having substituents attached to the side wall of the nanotube by reacting single wall carbon nanotubes with fluorine gas and recovering fluorine derivatized carbon nanotubes, then reacting fluorine derivatized carbon nanotubes with a nucleophile. Some of the fluorine substituents are replaced by nucleophilic substitution. If desired, the remaining fluorine can be completely or partially eliminated to produce single wall carbon nanotubes having substituents attached to the side wall of the nanotube. The substituents will, of course, be dependent on the nucleophile, and preferred nucleophiles include alkyl lithium species such as methyl lithium. Alternatively, fluorine may be fully or partially removed from fluorine derivatized carbon nanotubes by reacting the fluorine derivatized carbon nanotubes with various amounts of hydrazine, substituted hydrazine or alkyl amine.

This invention also provides a process for preparing a suspension or solution of single wall carbon nanotubes in various solvents from which individual single wall carbon nanotubes may be isolated, the process comprising providing a mass of single wall carbon nanotubes that include bundles of fibers held in close association by van der Waals forces, derivatizing the side walls of the single wall carbon nanotubes with a plurality of chemical moieties distributed substantially uniformly along the length of said single wall carbon nanotube side walls, said chemical moieties having chemical and steric properties sufficient to prevent the reassembly of van der Waals force bound bundles, producing true solutions and recovering the individual, derivatized single wall carbon nanotubes from said solution or suspension. Preferably, the attached chemical moieties are fluorine to provide solution in various alcohols, preferably isopropyl alcohol, and various R-groups to appropriate to provide solubility in other solvents including $CHCl_3$, Dimethylformamide, etc.

In another embodiment, a method for forming a macroscopic molecular array of tubular carbon molecules is disclosed. This method includes the steps of providing at least about 10^6 tubular carbon molecules of substantially similar length in the range of 50 to 500 nm; introducing a linking moiety onto at least one end of the tubular carbon molecules; providing a substrate coated with a material to which the linking moiety will attach; and contacting the tubular carbon molecules containing a linking moiety with the substrate.

The present invention also provides seed materials for growth of single wall carbon nanotubes comprising a plurality of single wall carbon nanotubes or short tubular molecules having a catalyst precursor moiety covalently bound or physisorbed on the outer surface of the sidewall to provide the optimum metal cluster size under conditions that result in migration of the metal moiety to the tube end.

This invention also provides a seed array for the catalytic production of assemblies of single wall carbon nanotubes comprising a plurality of relatively short single wall carbon nanotubes assembled in a generally parallel configuration, and disposed on the side wall of each said single wall carbon nanotube a sufficient quantity of physisorbed or covalently bonded transition metal catalyst precursor moieties to provide active catalyst metal atom clusters of the proper size to grow single wall carbon nanotubes under conditions that promote the generation of metal atoms and the migration of said metal atoms to the free ends of said single wall carbon nanotubes.

In another embodiment, a method for continuously growing a macroscopic carbon fiber comprising at least about 10^6

single-wall nanotubes in generally parallel orientation is disclosed. In this method, a macroscopic molecular array of at least about 10^6 tubular carbon molecules in generally parallel orientation is provided. The array is processed to provide a single plane of open-ended nanotubes at an angle generally perpendicular to the axes of parallel tubes in the array. The open ends of the tubular carbon molecules in the array are then contacted with a catalytic metal by causing migration of metal atoms released from side wall attached catalyst precursor groups. A gaseous source of carbon is supplied to the end of the array while localized energy is applied to the end of the array in order to heat the end to a temperature in the range of about 500°C . to about 1300°C . The growing carbon fiber is continuously recovered.

In another embodiment, an apparatus for forming a continuous macroscopic carbon fiber from a macroscopic molecular template array similar to that described above, comprising at least about 10^6 single-wall carbon nanotubes having a catalytic metal deposited on the open ends of said nanotubes is disclosed. This apparatus includes a means for locally heating only the open ends of the nanotubes in the template array in a growth and annealing zone to a temperature in the range of about 500°C . to about 1300°C . It also includes a means for supplying a carbon-containing feedstock gas to the growth and annealing zone immediately adjacent the heated open ends of the nanotubes in the template array. It also includes a means for continuously removing growing carbon fiber from the growth and annealing zone while maintaining the growing open end of the fiber in the growth and annealing zone.

The foregoing objectives, and others apparent to those skilled in the art, are achieved according to the present invention as described and claimed herein, and in the text of U.S. provisional application No. 60/106,918, filed Nov. 3, 1998, which is incorporated herein in its entirety.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1. A) TEM image of pure, unreacted SWNT B) TEM of SWNT after being fluorinated at 325°C . C) TEM of SWNT after being fluorinated at 500°C . D) another TEM of SWNT fluorinated at 500°C . showing the formation of MWNT.

FIG. 2. Raman spectrum of pure, unreacted carbon SWNT.

FIG. 3. Raman spectra of SWNT fluorinated at A) 250°C . B) 325°C . and C) 400°C .

FIG. 4. Raman spectra showing the defluorination of the nanotubes originally fluorinated at A) 250°C . B) 325°C . and C) 400°C .

FIG. 5. A) SEM of pure, unreacted SWNT B) SEM of SWNT after having been fluorinated at 325°C . for 5 hours C) SEM of SWNT fluorinated at 325°C . and then defluorinated in hydrazine.

FIG. 6. A) Raman spectrum of SWNT after being fluorinated and then methylated. B) Raman spectrum of the pyrolyzed methylated. SWNT which looks exactly like the Raman spectrum of untreated. SWNT.

FIG. 7. B) EI mass spectrum of products given off during the pyrolysis of methylated SWNT. This spectrum corresponds to a probe temperature of $\sim 400^\circ\text{C}$.

FIG. 8. A) Infrared spectrum of the product of a 3 hour methylation reaction B) Infrared spectrum of the product of a 12 hour methylation reaction.

FIG. 9 shows a SEM image of purified SWNTs.

FIG. 10A shows an AFM image of fluorotubes which have been dissolved in 2-butanol and dispersed on mica.

FIG. 10B shows a typical height analysis of the scan in FIG. 2A, revealing the tube diameters to be on the order of 1.2–1.4 nm, values on the order of those determined previously for this product using TEM and XRD.

FIG. 11 shows a UV spectrum of fluorotubes solvated in 2-propanol after sonication times of A) 10 min. B) 40 min. and C) 130 min.

FIG. 12A shows an AFM image of fluorotubes after having been defluorinated with N_2H_4 , filtered, resuspended in DMF and dispersed on mica.

FIG. 12B shows an AFM image of untreated SWNTs dispersed on mica.

FIG. 13A shows a Raman spectrum of pure, untreated SWNTs.

FIG. 13B shows a Raman spectrum of fluorotubes.

FIG. 13C shows a Raman spectrum of fluorotubes after having been defluorinated with N_2H_4 . * denotes Ar plasma line.

FIG. 14 is a schematic representation of a portion of an homogeneous SWNT molecular array according to the present invention.

FIG. 15 is a schematic representation of an heterogeneous SWNT molecular array according to the present invention.

FIG. 16 is a schematic representation of the growth chamber of the fiber apparatus according to the present invention.

FIG. 17 is a schematic representation of the pressure equalization and collection zone of the fiber apparatus according to the present invention.

FIG. 18 is a composite array according to the present invention.

FIG. 19 is a composite array according to the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Carbon has from its very essence not only the propensity to self-assemble from a high temperature vapor to form perfect spheroidal closed cages (of which C_{60} is prototypical), but also (with the aid of a transition metal catalyst) to assemble into perfect single-wall cylindrical tubes which may be sealed perfectly at both ends with a semifullerene dome. These tubes, which may be thought of as one-dimensional single crystals of carbon, are true fullerene molecules.

Single-wall carbon nanotubes are much more likely to be free of defects than multi-wall carbon nanotubes. Defects in single-wall carbon nanotubes are less likely than defects in multi-walled carbon nanotubes because the latter have neighboring walls that provide for easily-formed defect sites via bridges between unsaturated carbon valences in adjacent tube walls. Since single-wall carbon nanotubes have fewer defects, they are stronger, more conductive, and therefore more useful than multi-wall carbon nanotubes of similar diameter.

Carbon nanotubes, and in particular the single-wall carbon nanotubes, are useful for making electrical connectors in micro devices such as integrated circuits or in semiconductor chips used in computers because of the electrical conductivity and small size of the carbon nanotube. The carbon nanotubes are useful as antennas at optical frequencies, and as probes for scanning probe microscopy such as are used in scanning tunneling microscopes (STM) and atomic force microscopes (AFM). The carbon nanotubes may be used in

place of or in conjunction with carbon black in tires for motor vehicles. The carbon nanotubes are also useful as supports for catalysts used in industrial and chemical processes such as hydrogenation, reforming and cracking catalysts.

Ropes of single-wall carbon nanotubes will conduct electrical charges with a relatively low resistance. Ropes are useful in any application where an electrical conductor is needed, for example as an additive in electrically conductive paints or in polymer coatings or as the probing tip of an STM.

In defining carbon nanotubes, it is helpful to use a recognized system of nomenclature. In this application, the carbon nanotube nomenclature described by M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullereness and Carbon Nanotubes*, Chap. 19, especially pp. 756-760, (1996), published by Academic Press, 525 B Street, Suite 1900, San Diego, Calif. 92101-4495 or 6277 Sea Harbor Drive, Orlando, Fla. 32877 (ISBN 0-12-221820-5), which is hereby incorporated by reference, will be used. The single wall tubular fullerenes are distinguished from each other by double index (n,m) where n and m are integers that describe how to cut a single strip of hexagonal "chicken-wire" graphite so that it makes the tube perfectly when it is wrapped onto the surface of a cylinder and the edges are sealed together. When the two indices are the same, $m=n$, the resultant tube is said to be of the "arm-chair" (or n,n) type, since when the tube is cut perpendicular to the tube axis, only the sides of the hexagons are exposed and their pattern around the periphery of the tube edge resembles the arm and seat of an arm chair repeated n times. Arm-chair tubes are a preferred form of single-wall carbon nanotubes since they are metallic, and have extremely high electrical and thermal conductivity. In addition, all single-wall nanotubes have extremely high tensile strength.

Carbon nanotubes may have diameters ranging from about 0.6 nanometers (nm) for a single-wall carbon nanotube up to 3 nm, 5 nm, 10 nm, 30 nm, 60 nm or 100 nm for single-wall or multi-wall carbon nanotubes. The carbon nanotubes may range in length from 50 nm up to 1 millimeter (mm), 1 centimeter (cm), 3 cm, 5 cm, or greater. The yield of single-wall carbon nanotubes in the product made by this invention is unusually high.

Catalytic Formation of Carbon Nanotubes

As will be described further, one or more transition metals of Group VIB chromium (Cr), molybdenum (Mo), tungsten (W) or Group VIII B transition metals, e.g., iron (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt) catalyze the growth of a carbon nanotube and/or ropes when contacted with a carbon bearing gas such as carbon monoxide and hydrocarbons, including aromatic hydrocarbons, e.g., benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene, anthracene or mixtures thereof, non-aromatic hydrocarbons, e.g., methane, ethane, propane, ethylene, propylene, acetylene or mixtures thereof; and oxygen-containing hydrocarbons, e.g., formaldehyde, acetaldehyde, acetone, methanol, ethanol or mixtures thereof. Mixtures of one or more Group VIB or VIII B transition metals also selectively produce single-wall carbon nanotubes and ropes of single-wall carbon nanotubes in higher yields. The mechanism by which the growth in the carbon nanotube and/or rope is accomplished is not completely understood. However, it appears that the presence of the one or more Group VI B or VIII B transition metals on the end of the carbon nanotube facilitates the addition of carbon from the carbon vapor to the solid structure that

forms the carbon nanotube. Applicants believe this mechanism is responsible for the high yield and selectivity of single-wall carbon nanotubes and/or ropes in the product and will describe the invention utilizing this mechanism as merely an explanation of the results of the invention. Even if the mechanism is proved partially or wholly incorrect, the invention which achieves these results is still fully described herein.

One aspect of the invention comprises a method of making carbon nanotubes and/or ropes of carbon nanotubes which comprises supplying carbon vapor to the live end of one or more of a carbon nanotubes growing by a catalytic process in which there is a "live end" of the nanotube in contact with a nanometer-scale transition metal particle that serves as a catalyst. The live end of the nanotube is maintained in contact with a carbon bearing feedstock gas in an annealing zone at an elevated temperature. In one process of this type carbon in vapor form may be supplied in accordance with this invention by an apparatus in which a laser beam impinges on a target comprising carbon that is maintained in a heated zone. A similar apparatus has been described in the literature, for example, in U.S. Pat. No. 5,300,203, or in PCT/US96/14188, both of which are incorporated herein by reference, and in Chai, et al., "Fullerenes with Metals Inside," *J. Phys. Chem.*, vol. 95, no. 20, p. 7564 (1991). Alternatively carbon may be added to the live end by the direct action of the catalytic particle in the annealing zone with a carbon-bearing feedstock gas such as carbon monoxide and hydrocarbons, including aromatic hydrocarbons, e.g., benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene, anthracene or mixtures thereof, non-aromatic hydrocarbons, e.g., methane, ethane, propane, ethylene, propylene, acetylene or mixtures thereof; and oxygen-containing hydrocarbons, e.g., formaldehyde, acetaldehyde, acetone, methanol, ethanol or mixtures thereof.

According to this invention, a "live end" can also be produced on a carbon nanotube derivatized with chemical moieties which bind Group VI B or Group VIII B metal to the tube. This mode is discussed in greater detail below. Additional carbon vapor is then supplied to the live end of a carbon nanotube under the appropriate conditions to increase the length of the carbon nanotube.

The carbon nanotube that is formed is not always a single-wall carbon nanotube; it may be a multi-wall carbon nanotube having two, five, ten or any greater number of walls (concentric carbon nanotubes). Preferably, though, the carbon nanotube is a single-wall carbon nanotube, and this invention provides a way of selectively producing single-wall carbon nanotubes in greater and sometimes far greater abundance than multi-wall carbon nanotubes.

Elongation of Single-wall Nanotubes

As contemplated by this invention, growth or elongation of single-wall carbon nanotubes requires that carbon in vapor form be supplied to the live end of the growing nanotube in an annealing zone. In this application, the term "live end" of a carbon nanotube refers to the end of the carbon nanotube on which catalytic amounts of one or more Group VI B or VIII B transition metals are located. The catalyst should be present on the open SWNT ends as a metal cluster containing from about 10 metal atoms up to about 200 metal atoms (depending on the SWNT molecule diameter). Preferred are metal clusters having a cross-section equal to from about 0.5 to about 1.0 times the tube diameter (e.g., about 0.7 to 1.5 nm).

A carbon nanotube having a live end will grow in length by the catalytic addition of carbon from the vapor to the live

end of the carbon nanotube if the live end is placed in an annealing zone and then additional carbon-containing vapor is supplied to the live end of the carbon nanotube. The annealing zone where the live end of the carbon nanotube is initially formed should be maintained at a temperature of 500° to 1500° C., more preferably 1000° to 1400° C. and most preferably 1100 to 1300° C. In embodiments of this invention where carbon nanotubes having live ends are caught and maintained in an annealing zone and grown in length by further addition of carbon (without the necessity of adding further Group VI B or VIII B transition metal vapor), the annealing zone may be cooler, 400° to 1500° C., preferably 400° to 1200° C., most preferably 500° to 700° C. The pressure in the annealing zone should be maintained in the range of pressure appropriate to the catalyst/feedstock system being used, i.e., 50 to 2000 Torr., more preferably 100 to 800 Torr, and most preferably 300 to 600 Torr in the case of carbon or hydrocarbon gasses, but up to 100 atmospheres in the case of CO feedstock. The atmosphere in the annealing zone will contain carbon in some form. Normally, the atmosphere in the annealing zone will also comprise a gas that sweeps the carbon vapor through the annealing zone to a collection zone. Any gas that does not prevent the formation of carbon nanotubes will work as the sweep gas, but preferably the sweep gas is an inert gas such as helium, neon, argon, krypton, xenon, or mixtures of two or more of these. Helium and Argon are most preferred. The use of a flowing inert gas provides the ability to control temperature, and more importantly, provides the ability to transport carbon to the live end of the carbon nanotube. In some embodiments of the invention, when other materials are being vaporized along with carbon, for example one or more Group VI B or VIII B transition metals, those compounds and vapors of those compounds will also be present in the atmosphere of the annealing zone. If a pure metal is used, the resulting vapor will comprise the metal. If a metal oxide is used, the resulting vapor will comprise the metal and ions or molecules of oxygen.

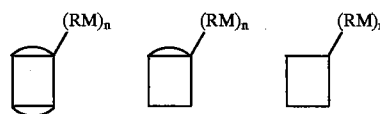
It is important to avoid the presence of too many materials that kill or significantly decrease the catalytic activity of the one or more Group VI B or VIII B transition metals at the live end of the carbon nanotube. It is known that the presence of too much water (H₂O) and/or oxygen (O₂) will kill or significantly decrease the catalytic activity of the one or more Group VI B or VIII B transition metals. Therefore, water and oxygen are preferably excluded from the atmosphere in the annealing zone. Ordinarily, the use of a sweep gas having less than 5 wt %, more preferably less than 1 wt % water and oxygen will be sufficient. Most preferably the water and oxygen will be less than 0.1 wt %.

The carbon-containing vapor supplied to the live end in the annealing zone may be provided by evaporation of a solid carbon target using energy supplied by an electric arc or laser, as described herein. However, once the single-wall carbon nanotube having a live end is formed, the live end will catalyze growth of the single-wall carbon nanotube at lower temperatures and with other carbon sources. An alternative carbon source for growing the SWNT may be fullerenes, that can be transported to the live end by the flowing sweep gas. The carbon source can be graphite particles carried to the live end by the sweep gas. The carbon source can be a hydrocarbon that is carried to the live end by a sweep gas or a hydrocarbon gas or mixture of hydrocarbon gasses introduced into the annealing zone. Hydrocarbons useful include methane, ethane, propane, butane, ethylene, propylene, benzene, toluene or any other paraffinic, olefinic, cyclic or aromatic hydrocarbon, or any other hydrocarbon.

Another alternative that may be used as a source of carbon-containing vapor are other gaseous compounds that can form elemental carbon by disproportionation such as CO, C₂F₄ and C₂H₄.

Chemically Modified Carbon Nanotubes

The present invention provides carbon nanotubes having chemically derivatized side walls. In preferred embodiments, the derivatization facilitates formation of more complex functional compounds with carbon nanotubes. Derivatization also enables complexing of Group VI B and/or Group VIII B metals on the nanotubes. In particularly preferred embodiments, the derivatized nanotubes are derivatized molecular growth precursors of this invention which may have the following structures and functions:



where



is a substantially defect-free cylindrical graphene sheet (which optionally can be doped with non-carbon atoms) having from about 10² to about 10⁷ carbon atoms, and having a length of from about 5 to about 10000 nm, preferably about 5 to about 500 nm;



is a fullerene cap that fits perfectly on the cylindrical graphene sheet, has at least six pentagons and the remainder hexagons and typically has at least about 30 carbon atoms;

M is a group VI B or VIII B metal;

n is a number from 10–100000, preferably 50 to 20000; and

R is a linking or complexing moiety that can include groups selected from the group consisting of alkyl, acyl, aryl, aralkyl, halogen; substituted or unsubstituted thiol; unsubstituted or substituted amino; hydroxy, and OR' wherein R' is selected from the group consisting of hydrogen, alkyl, acyl, aryl aralkyl, unsubstituted or substituted amino; substituted or unsubstituted thiol; and halogen; and a linear or cyclic carbon chain optionally interrupted with one or more heteroatom, and optionally substituted with one or more =O, or =S, hydroxy, an aminoalkyl group, an amino acid, or a peptide of 2–8 amino acids.

Other embodiments of the derivatized nanotubes of this invention have structures as described above, except metal is not present and the R group does not necessarily serve to form complexes. The following definitions are used herein.

The term "alkyl" as employed herein includes both straight and branched chain radicals, for example methyl, ethyl, propyl, isopropyl, butyl, t-butyl, isobutyl, pentyl, hexyl, isohexyl, heptyl, 4,4-dimethylpentyl, octyl, 2,2,4-trimethylpentyl, nonyl, decyl, undecyl, dodecyl, the various branched chain isomers thereof. The chain may be linear or cyclic, saturated or unsaturated, containing, for example, double and triple bonds. The alkyl chain may be interrupted

or substituted with, for example, one or more halogen, oxygen, hydroxy, silyl, amino, or other acceptable substituents.

The term "acyl" as used herein refers to carbonyl groups of the formula —COR wherein R may be any suitable substituent such as, for example, alkyl, aryl, aralkyl, halogen; substituted or unsubstituted thiol; unsubstituted or substituted amino, unsubstituted or substituted oxygen, hydroxy, or hydrogen.

The term "aryl" as employed herein refers to monocyclic, bicyclic or tricyclic aromatic groups containing from 6 to 14 carbons in the ring portion, such as phenyl, naphthyl, substituted phenyl, or substituted naphthyl, wherein the substituent on either the phenyl or naphthyl may be for example C₁₋₄ alkyl, halogen, C₁₋₄ alkoxy, hydroxy or nitro.

The term "aralkyl" as used herein refers to alkyl groups as discussed above having an aryl substituent, such as benzyl, p-nitrobenzyl, phenylethyl, diphenylmethyl, and triphenylmethyl.

The term "aromatic or non-aromatic ring" as used herein includes 5–8 membered aromatic and non-aromatic rings uninterrupted or interrupted with one or more heteroatom, for example O, S, SO, SO₂, and N, or the ring may be unsubstituted or substituted with, for example, halogen, alkyl, acyl, hydroxy, aryl, and amino, said heteroatom and substituent may also be substituted with, for example, alkyl, acyl, aryl, or aralkyl.

The term "linear or cyclic" when used herein includes, for example, a linear chain which may optionally be interrupted by an aromatic or non-aromatic ring. Cyclic chain includes, for example, an aromatic or non-aromatic ring which may be connected to, for example, a carbon chain which either precedes or follows the ring.

The term "substituted amino" as used herein refers to an amino which may be substituted with one or more substituent, for example, alkyl, acyl, aryl, aralkyl, hydroxy, and hydrogen.

The term "substituted thiol" as used herein refers to a thiol which may be substituted with one or more substituent, for example, alkyl, acyl, aryl, aralkyl, hydroxy, and hydrogen.

Typically, open ends may contain up to about 20 substituents and closed ends may contain up to about 30 substituents. It is preferred, due to steric hindrance, to employ up to about 12 substituents per end.

In addition to the above described external derivatization, the SWNT molecules of the present invention can be modified endohedrally, i.e., by including one or more other atoms or molecules inside the structure, as is known in the endohedral fullerene art.

To produce endohedral tubular carbon molecules, the internal species (e., metal atom) can either be introduced during the SWNT formation process or added after preparation of the nanotubes.

Endohedrally loaded tubular carbon molecules can then be separated from empty tubes and any remaining loading materials by taking advantage of the new properties introduced into the loaded tubular molecules, for example, where the metal atom imparts magnetic or paramagnetic properties to the tubes, or the bucky ball imparts extra mass to the tubes. Separation and purification methods based on these properties and others will be readily apparent to those skilled in the art.

Derivatization of SWNT Sidewalls with Fluorine

Since the discovery of single wall carbon nanotubes (SWNT) Iijima, et al. (1993), there has been a flurry of research activity aimed at understanding their physical properties (Issi, et al. (1995), *Carbon*, 33:941–948), elucidating

their growth mechanisms (Cornwell, et al. (1997), *Chem. Phys. Lett.*, 278:262–266), and developing novel uses for them (Dillon, et al. (1997), *Nature*, 386:377–389). Chemistry involving SWNT is still in its infancy. This is due, in large part, to previous difficulties in obtaining reasonable quantities of highly purified SWNT.

Progress in the bulk synthesis and purification (Rinzler, et al., 1998, *App. Phys. A*, 67:29–37) of SWNT is now making available high quality samples in sufficient quantities to begin exploring the chemical modification of this fascinating class of materials. Recently, sono-chemistry was employed to cut the long, intertwined tubes into independent, macro-molecular scale, open tube fragments (50–300 nm long) (Liu, et al., 1998). In that work, the high reactivity of the-dangling carbon bonds at the open tube ends was exploited to tether the tubes to gold particles via thiol linkages.

In contrast to the open tube ends, the side-walls of the SWNT, by virtue of their aromatic nature, possess a chemical stability akin to that of the basal plane of graphite (Aihara, 1994, *J. Phys. Chem.*, 98:9773–9776). The chemistry available for modification of the nanotube side-wall (without disruption of the tubular structure) is thus significantly more restrictive. However, the present inventors have adapted technology developed in the fluorination of graphite (see, eg., Lagow, et al., 1974, *J. Chem. Soc., Dalton Trans.*, 12:1268–1273) to the chemical manipulation of the SWNT side-wall by fluorinating high purity SWNT and then defluorinating them. Once fluorinated, single-wall carbon nanotubes can serve a staging point for a wide variety of side-wall chemical functionalizations, in a manner similar to that observed for fluorinated fullerenes (see Taylor, et al., 1992, *J. Chem. Soc., Chem. Comm.*, 9:665–667, incorporated herein by reference).

According to the present invention, single-wall carbon nanotubes are derivatized by exposure to a fluorinating agent, which may be fluorine gas or any other well known fluorinating agent such as XeF₂, XeF₄, ClF₃, BrF₃, or IF₅. XeF₂, and XeF₄ may be advantageous, being free of HF. Alternatively, solid fluorinating agents, such as AgF₂ or MnF₃, may be reacted in slurry with SWNT.

Purified single wall carbon nanotubes (SWNT) were fluorinated by the inventors by treatment with F₂ at several different temperatures and concentrations using various mixtures of about 5% F₂ in a one-atmosphere pressure mixture with rare gases, including He and Ar. The reactor temperature was between 150° C. and 400° C. Infrared spectroscopy was used to verify the existence of covalent carbon-fluorine bonds. Product stoichiometries were determined and transmission electron microscopy (TEM) was used to verify whether or not the fluorination was destructive of the tubes. SWNT fluorinated at three different temperatures were then defluorinated using hydrazine. Raman spectroscopy was used to verify whether or not the products of the defluorination were in fact SWNT. It was determined, via scanning electron microscopy (SEM) and two-point resistance measurements, that the bulk of the SWNT survive the fluorination process at temperatures up to 325° C. and that the fluorine can be effectively removed from the tubes with hydrazine to regenerate the unfluorinated starting material.

Not unexpectedly, the electronic properties of the fluorinated tubes differ dramatically from those of their unfluorinated counterparts. While the untreated SWNT are good conductors (10–15Ω two probe resistance across the length of the ~10×3 mm×30 μm bucky paper samples), the tubes fluorinated at temperatures of 250° C. and above are insulators (two probe resistance >20 MΩ).

Gravimetric and electron microprobe analysis demonstrated that large amounts of fluorine can be added to SWNT. Resistance measurements along with vibrational spectroscopy (Raman, IR) confirm the formation of new chemical bonds to the nanotube superstructure. Contributions of absorbed molecular fluorine to the overall fluorine uptake are precluded at these temperatures (Watanabe, et al., 1988). It may be concluded, therefore, that fluorine is being covalently attached to the side wall of the SWNT.

TEM studies have shown that at fluorination temperatures as high as 325° C., the majority of the fluorination product maintains a tube-like structure. These studies also indicate that at 500° C., the single wall tubular structure does not survive the fluorination process and that some MWNT-like structures are being formed.

From the product stoichiometries, resistance measurements and IR spectra it is clear that reaction temperatures in excess of 150° C. allow one to covalently add significant amounts of fluorine to the tube wall. The small amount of fluorine that does show up in the product of the 150° C. fluorination reaction could be attributed to a combination of absorbed fluorine and fluorination of the end caps of the SWNT.

Fluoride can also be effectively removed from the SWNT using anhydrous hydrazine and that the rejuvenated product is in fact a SWNT. The inventors have found that, once fluorinated, SWNT can be defluorinated with anhydrous hydrazine via the following reaction: $CF_n + (n/4)N_2H_4 \rightarrow C + nHF + (n/4)N_2$. From the results of these defluorination experiments and the Raman and SEM studies associated with them, it appears that a majority of the tubes are destroyed at fluorination temperatures of above 400° C., whereas only a slight amount of tube destruction occurs at 250° C.

For reactions in which only the outside of the tube is being fluorinated (the SWNT used in this study were closed at the ends), there is a limiting stoichiometry of C_2F for which the fluorinated tube can still maintain its tube-like (albeit puckered) structure. This is supported by the product stoichiometries obtained via elemental analysis and the evidence of significant tube destruction at fluorination temperatures greater than 325° C. Further addition of fluorine would then lead to the breaking of carbon-carbon bonds and, hence, destruction of the tube. Accordingly, this invention provides a method of derivatizing SWNT with F_2 to add fluorine substituents to the exterior of the sidewalls in stoichiometries of up to C_2F , although lesser amounts of fluorine can also be attached by further diluting the fluorine or by lowering the reaction temperature.

Changing the Derivatization of SWNT by Fluorine Substitution

Because the inertness of the SWNT side wall approximates that of the basal plane of graphite, chemistry involving the SWNT side wall may be quite limited. However, the present invention provides methods for fluorination of single wall carbon nanotubes (SWNTs) where fluorine is covalently bound to the side wall of the nanotube and thus provide sites for chemical reactions to occur. Functionalization via a fluorinated precursor may thus provide an attractive route to a wide range of side wall derivatizations.

In a particular embodiment, highly purified single wall carbon nanotubes (SWNTs) may be fluorinated to form "fluorotubes" which can then be solvated as individual tubes. For example, fluorotubes may be solvated in various alcohol solvents via ultrasonication. The solvation of individual fluorotubes has been verified by dispersing the solvated tubes on a mica substrate and examining them with

atomic force microscopy (AFM). Elemental analysis of the tubes reveals that light sonication in alcohol solvents does not remove significant amounts of the fluorine. These solutions will persist long enough (over a week) to permit solution phase chemistry to be carried out on the fluorotubes. For example, the solvated fluorotubes can be treated with hydrazine to remove fluorine, leading to precipitation from solution of normal, unfluorinated SWNTs. Alternatively, fluorotubes can be reacted with sodium methoxide to yield methoxylated SWNTs. These reaction products have also been characterized by elemental analysis and a variety of spectroscopies and microscopies.

The present inventors have, for the first time, functionalized the sidewalls of SWNTs by reacting them with elemental fluorine. The inventors have discovered that fluorine could be added to the side wall of carbon nanotubes yielding stoichiometries up to approximately C_2F without destruction of the tube-like structure. The inventors have also discovered that a high degree of solvation can be achieved by sonicating fluorinated SWNTs in a variety of alcohol solvents such as methanol, ethanol, and isopropanol. As demonstrated herein, reactions can be carried out on these nanotubes while in solution by reacting them with hydrazine which serves as a defluorinating agent. It has also been demonstrated that these "fluorotubes" can be reacted with sodium methoxide (a strong nucleophile) while in solution to form methoxylated SWNTs.

The inventors have shown that single wall carbon nanotubes can be fluorinated and then sonicated in alcohols to form stable solutions of fluorotubes. This solvation allows one to manipulate the fluorotubes in ways that were previously unavailable and opens the door to a wide variety of possibilities with respect to exploring the physical and chemical properties of fluorotubes. "Tuning" the fluorine content of a fluorotube by first fluorinating it heterogeneously, solvating it in an alcohol, and then defluorinating it with substoichiometric quantities of hydrazine is consequently available as a way of making a wide variety of fluorotubes with differing fluorine contents and in some instances quite different properties.

The inventors have further demonstrated that once solvated, these fluorotubes can then be reacted with species while in solution to either defluorinate or further functionalize them. The chemistry possible with these solvated fluorotubes provides an important route to the synthesis of a wide variety of functionalized nanotubes having many different and useful properties.

An exemplary derivatization is the methylation of SWNT. Methylated SWNT are the product of the nucleophilic substitution of fluorine (attached to the SWNT side wall) by the methyl groups in methyl lithium. Nucleophilic substitution of this type has been previously reported for the reaction between fluorinated C_{60} and alkyl lithium species (Taylor, et al., 1992). The C—F bonds in fullerene cages and tubes are weakened relative to C—F bonds in alkyl fluorides by an eclipsing strain effect (Taylor, 1998 *Russian Chem. Bull.*, 47:823–832). This renders the bonds more susceptible to nucleophilic attack. A normal S_N2 process is geometrically impossible and a S_N1 process would be extremely unlikely, so either a novel front side displacement or possibly an addition-elimination process is responsible for the nucleophilic substitution (See Taylor, 1995, in "The Chemistry of Fullerenes," R. Taylor, ed., world Scientific Publishing, London, pp.208–209).

EXAMPLES

Example 1

1.1 Fluorination of Single-wall Carbon Nanotubes

Single-walled carbon nanotubes were produced by the dual pulsed laser vaporization of Co/Ni doped graphite rods and purified by techniques described previously (Rinzler, et al., 1998). The purification product is a metastable colloidal suspension of SWNT "ropes" (bundles of hexagonally close packed tubes ranging from a few to 200 SWNT, See Thess, et al., 1996) in a 0.2% aqueous solution of Triton X-100 surfactant. Filtering the solution through a PTFE filter membrane and washing with methanol to remove residual surfactant leaves a black film on the surface. If this layer is sufficiently thick (10–75 μm) it can be peeled off to form a free standing film or "bucky paper" of SWNT. This form has appreciable mechanical integrity and is convenient for handling, and for electrical conductivity and Raman scattering measurements. It is the fluorination of this "bucky paper" that is described here.

In fluorinating the SWNT, elemental fluorine (Air Products, 98%) was used as the fluorinating agent. HF, being the major impurity in the fluorine, was removed by passing it through an HF trap (Matheson Gas Products) containing sodium fluoride pellets. The fluorine, diluted with helium (Trigas, 99.995%), was then passed through a temperature-controlled Monel flow reactor containing the SWNT sample.

Prior to fluorination, the purified "bucky paper" was vacuum baked at 1100° C. (2×10^{-6} Torr) for several hours in order to desorb any residual surface contaminants. For each reaction a pre-weighed piece of "bucky paper" (weighing 150–200 μg) was used. F_2 and He flow rates for each reaction were 2 sccm and 20 sccm, respectively. In each case the reaction time was 5 hours. The only variable was reaction temperature. As the kinetics of inorganic carbon+fluorine reactions are highly temperature dependent (Watanabe, et al., 1988, "Graphite fluorides," Elsevier, Amsterdam), several reactions were carried out at the following temperatures: 150° C., 250° C., 325° C., 400° C., 500° C. and 600° C. At reaction temperatures of 325° C. and 400° C., the fluorination was begun at 250° C. and after one hour, the F_2 flow was stopped and the reactor temperature brought up to the appropriate level for an additional 4 hours. For the reactions at 500° C. and 600° C., the sample was fluorinated for 1 hour at 250° C., 1 hour at 400° C. and then 3 hours at the specified reaction temperature. The rationale behind this "stepped reaction temperature procedure" was to minimize, as much as possible, the decomposition: CF_4 , C_2F_4 , C_2F_6 , etc. which has been well documented in the fluorination of graphite (Kamarchik, et al., 1978, *Acc. Chem. Res.*, 11:196–300) and fullerenes (Selig, et al., 1991, *J. Am. Chem. Soc.*, 113:5475–5476).

Product stoichiometries as a function of reaction temperature were obtained both gravimetrically (TA Instruments TGA-DTA 2960 microbalance) and via electron microprobe analysis (Cameca SX 50). Infrared spectroscopy (Perkin-Elmer Paragon 1000 FT-IR) was used to confirm the presence of covalently bound fluorine. Transmission electron microscopy (JEOL model 2010 TEM using 100 keV beam energy) was used to determine if, and at what temperature the tubes were being destroyed (i.e., unzipped) by the fluorination. Raman spectroscopy (Jobin Yvon-Spex model HR460 monochromator coupled with an ISA Spectrum ONE series CCD detector and using a 532 nm Nd:YAG laser excitation source), scanning electron microscopy (JEOL model JSM-6320F field emission SEM using 5 keV beam energy) and two-point resistivity measurements were used to analyze the untreated, fluorinated and defluorinated SWNT samples.

Infrared spectroscopy (KBr pellet method) confirmed the presence of covalently bound fluorine (peaks in the 1220–12.50 cm^{-1} region) in the samples fluorinated, at temperatures of 250° C. and higher. No C-F stretching frequency was seen for the sample fluorinated at 150° C. and its two-point resistance (5 mm apart) was ~ 100 which therefore precludes large amounts of fluorine being covalently bound to the SWNT side wall. Product stoichiometries of the fluorination reactions are shown in Table 1. Discrepancies between the gravimetric and microprobe analyses can be attributed to product decomposition as described above, especially at the higher temperatures.

FIG. 1-A shows a TEM image of the purified, unreacted SWNT material. FIG. 1-B shows a TEM image of SWNT fluorinated at 325° C. As can be seen from the image, the tubes remain largely intact after treatment under these conditions. FIG. 1-C is a TEM image of SWNT fluorinated at 500° C. Here it would appear that the tubes are essentially all destroyed. However, a fair number of nested tube-like graphic structures reminiscent of multiwall carbon nanotubes (MWNT) seem to have been generated as a result of the high temperature reaction. These structures are shown in FIG. 1-D.

The fluorination of MWNT has been reported previously (Hamwi, et al., 1997, *Carbon*, 35:723–728). This was done at two temperatures: 25° C. and 500° C. The room temperature reaction was done with a F_2 , HF and IF_5 mixture and yielded an intercalated type compound. The reaction carried out at 500° C. was done with F_2 , and was determined to have destroyed the tube structure to yield a graphite fluoride compound of stoichiometry CF. In light of this, it is not too surprising that destruction of the SWNT was observed at 500° C., but somewhat surprising that MWNT-like structures are formed. The generation of these may be a consequence of residual metal catalysts present in the sample.

TABLE 1

Reaction product stoichiometries determined by both gravimetric and electron microprobe analysis.

	Reaction temp. ° C.					
	150	250	325	400	500	600
gravimetric	$\text{CF}_{0.114}$	$\text{CF}_{0.521}$	$\text{CF}_{0.495}$	$\text{CF}_{0.565}$	*	
microprobe	$\text{CF}_{0.097}$	$\text{CF}_{0.458}$	$\text{CF}_{0.554}$	$\text{CF}_{0.647}$	$\text{CF}_{0.815}$	$\text{CF}_{0.99}$

* no determination at these temperatures.

1.2 Defluorination of Single-wall Carbon Nanotubes

Once fluorinated, SWNT were defluorinated with anhydrous hydrazine (Aldrich, 98%). To the pieces of "bucky paper", fluorinated at 250° C., 325° C. and 400° C., was added 5 ml of hydrazine under an inert atmosphere at room temperature. The SWNT were allowed to sit in the hydrazine for one hour prior to filtering and washing with water.

As the Raman spectroscopy of SWNT has been well developed both theoretically (Richter, et al., 1997, *Phys. Rev. Lett.*, 79:2738–2741) and experimentally (Rao, et al., 1998, *Science*, 275:187–191), it was used to examine the results of both the fluorination and subsequent defluorination of the SWNT. FIG. 2 shows the Raman spectrum of the pure, unadulterated SWNT material. The smaller peak at 186 cm^{-1} is due to a characteristic breathing mode of the SWNT. Raman spectra of SWNT fluorinated for 5 hours at reaction temperatures of 250° C., 325° C. and 400° C. are shown in FIG. 3. Trace A, corresponding to the reaction at 250° C., shows only two broad peaks centered around 1340 cm^{-1} and 1580 cm^{-1} and a broad band fluorescence. The Raman peaks

correspond to sp^3 and sp^2 carbon stretching modes, respectively. At higher reaction temps, yielding high F to C ratios, these peaks disappear and the fluorescence is attenuated. As C—F bonds are not very polarizable, it is understandable that they are not seen in the Raman spectra presented here.

Raman spectra of the defluorinated products of the SWNT originally fluorinated at 250° C., 325° C. and 400° C. are shown in FIG. 4. Traces A, B and C correspond to the material originally fluorinated at 250° C., 325° C. and 400° C., respectively. As can be seen in traces A and B, the characteristic breathing mode at 186 cm^{-1} returns upon defluorination. This is not true in trace C, indicating that the tubes are largely destroyed at 400° C. Additionally, the peak at 1340 cm^{-1} grows relative to the characteristic SWNT peaks with increasing fluorination temperature. This can be attributed to one or both of the following factors: one, tubes are being "funzipped" much more readily at the higher temperatures and secondly, at higher reaction temperatures, a greater amount of decomposition of the type: CF_4 , C_2F_4 , C_2F_6 , etc, is occurring. SEM images and two-point resistivity measurements were obtained on a single piece of "bucky paper" after each of the following stages: purification, fluorination at 325° C. and defluorination in hydrazine at room temperature for one hour. FIG. 5-A shows the purified starting material. FIG. 5-B shows the same piece after having been fluorinated at 325° C. for 5 hours. The image shows excessive charging due to its insulating nature, but the "rope-like" structure of tubes is still evident. Finally, FIG. 5-C shows the same piece of "bucky paper" after having been defluorinated in hydrazine. The two-point resistance of the purified starting material is 15–16 Ω measured 5 mm across the surface of the "bucky paper". Identical measurements on the fluorinated and defluorinated "bucky paper" yielded a resistance of >20 M Ω and 125–130 Ω respectively. It is interesting to note that the defluorinated material recovers most, but not all of its original conductivity.

Example 2

2.1 Preparation of Fluorinated Single-wall Carbon Nanotubes

SWNT were produced by the dual pulsed laser vaporization of Co/Ni doped graphite rods and purified as discussed previously (Rinzler, et al., 1998). The highly purified product consists of colloiddally suspended bundles or "ropes" of SWNT (Liu, et al., 1998). Filtering this over a 0.2 micron PTFE filter membrane and rinsing with methanol yields a black film that can be peeled off to give a freestanding "bucky paper." This paper was then oven baked for several hours at 150° C. to remove any residual solvent. The baked "bucky paper" was then loaded into a temperature controlled monel flow reactor where it was purged at 250° C. under a stream of He for ~1 hour. A 10% F_2 in He mixture was then passed over the sample after first being passed over NaF to remove any HF present. This yielded material with stoichiometries ranging from C_3F to C_2F (as determined by electron microprobe analysis) depending on reaction time (between 8 and 12 hours) and on the quantity being fluorinated.

2.2 Methylated Single-wall Carbon Nanotubes

Once fluorinated, the nanotubes were then placed in a reaction flask under a N_2 purge. Methyl lithium (1.4 M in diethyl ether, Aldrich) was then added in significant molar excess via syringe through a rubber septum in the reaction flask. The reaction mixture was then refluxed for three hours and after which, the methyl lithium was neutralized with a water/ether mixture. The resulting material was then filtered, washed with 3M HCl (to remove LiF and LiOH) followed by methanol and then oven dried at 130° C. Electron

microprobe analysis revealed the fluorine content of this material to be 3.7 atomic percent (down from around 30%). SEM and TEM analysis confirmed that the rope and tube structures survived both the fluorination and methylation steps.

The Raman spectroscopy of SWNT is now well known (Rao, et al., 1998). Raman spectroscopy of the methylated nanotube product was obtained on a Spex Triplemate spectrometer equipped with a CCD detector and using a 514.5 nm Ar laser excitation source. The spectrum reveals that significant alteration has taken place (FIG. 6). Pyrolysis of this material in Ar at 700° C. regenerates the original SWNT as evidenced by its Raman spectrum. TGA of the pyrolysis process reveals a 25% mass loss upon heating to 700° C. EI mass spectroscopy of the pyrolysis products reveals CH_3 groups to be the major species being evolved during the pyrolysis (FIG. 7) with the rest of the mass peaks being consistent with methyl recombination pathways during pyrolysis.

The electrical properties of the SWNT change dramatically as they are functionalized. The untreated SWNT are essentially metallic and their two point resistance (essentially a contact resistance, Bozhko, et al., 1998, *Appl. Phys. A*, 67:75–77) measured across 5 mm of the "bucky paper" surface is 10–15 Ω . When fluorinated, the tubes become insulating and the two point resistance exceeds 20 M Ω . After methylation the tubes possess a two point resistance of ~20 k Ω . Pyrolysis of the methylated product brings the resistance down to ~100 Ω . Incomplete return of the electrical conductivity upon pyrolysis may be due to an increased contact resistance that results from disorder induced into the rope lattice following the sequence of reaction steps.

The methylated SWNT could be suspended quite readily by sonication in chloroform. Dispersal of this suspension on a Si wafer followed by AFM analysis confirmed the non-destructive nature of the sonication process. Additionally, a large number of single tubes could be seen. This was not true of similarly exposed, untreated SWNT.

To get an infrared spectrum of the product, the dried methylated material was suspended in $CDCl_3$ and dispersed over KBr powder which was then dried and pressed into a pellet. By using deuterated chloroform we eliminated the possibility of seeing C—H stretching modes due to the presence of residual solvent. IR analysis of the pellet revealed a significant amount of C—H stretching in the ~2950 cm^{-1} region of the spectrum as shown in FIG. 8. Also present, however, is a significant C—F stretching band indicating that not all of the fluorine had been displaced. This might be because the bulky methyl lithium could not penetrate the rope lattice to the extent that the fluorine could in the original fluorination. Alternatively, the cage is likely to become less electronegative and, therefore, less susceptible to nucleophilic attack as successive fluorines are displaced (see Boltalina, et al., 1996, *J. Chem. Soc., Perkin Trans.*, 2:2275–2278).

The methylated tubes were not suspendable in any of the nonpolar hydrocarbon solvents tried, although not all possibilities were investigated. The fact that the suspendability of the methylated tubes in $CHCl_3$ is superior to that of the untreated tubes is interesting, however. Using a suitable solvent to suspend the methylated SWNT as individual tubes capable of being manipulated individually, will have significant benefits. Alternatively, other nucleophiles, e.g. butyl, can be substituted for the fluorine to render the SWNT more suspendable in a suitable solvent, which is equally significant.

In summary, SWNT were methylated by first fluorinating them and then reacting the fluorinated product with methyl lithium. This methylation of fluorinated SWNT precursors proceeds through a novel nucleophilic substitution pathway that is capable of generating a wide range of substituted SWNT products.

Example 3

3.1 Preparation of Highly Purified SWNTs

Single wall carbon nanotubes were produced by the dual pulsed laser vaporization of Co/Ni doped graphite rods and purified by methods discussed previously (Rinzler, et al., Appl. Phys. A, 1998, 67:9-37.). The SWNTs produced in this way are primarily (10,10) nanotubes. The purified product is a metastable colloidal suspension of SWNT "ropes" (bundles of tubes ranging from a few to 200 SWNTs, see Thess, et al., Science 1996, 273, 483-487) in a 0.2% aqueous solution of Triton™ X-100 surfactant. This was then filtered over a PTTE filter membrane (Sartorius, with 0.2 μ m pore dimensions) and rinsed with methanol. Filtering this and rinsing with methanol leads to a final product which is a freestanding "mat" or "bucky paper" of SWNTs that is approximately 10 μ m thick. Purity of the SWNTs was monitored via scanning electron microscopy (JEOL 6320F SEM). FIG. 9 shows a sample of typical purity. This product was then resuspended by sonication in dimethyl formamide (DMF; Fisher, HPLC grade). Such treatment is believed to "cut" the tubes at their defect sites and also seems to unravel the ropes somewhat, leading to bundles containing fewer SWNTs. This product was then filtered, rinsed and heated in an oven at 150° C. for 2 hours prior to fluorination. Sonication in DMF may result in smaller SWNT ropes and ultimately lead to a more efficient fluorination.

3.2 Preparation of Fluorinated SWNTs

The purified nanotubes (5-10 mg in the form of bucky paper) were placed in a temperature controlled fluorination reactor constructed of Monel™ and nickel. After sufficient purging in He (Trigas 99.995%) at 250° C., fluorine (Air Products 98%, purified of HF by passing it over NaF pellets) was introduced. The fluorine flow was gradually increased to a flow rate of 2 sccm diluted in a He flow of 20 sccm. The fluorination was allowed to proceed for approximately 10 hours, at which point the reactor was brought to room temperature, and the fluorine flow was gradually lowered. After the fluorine flow was completely halted, the reactor was purged at room temperature for approximately 30 minutes before removing the fluorinated product. The fluorinated SWNTs consisted of approximately 70 atomic percent carbon and 30 atomic percent fluorine as determined by electron microprobe analysis (EMPA, Cameca SX-50). This fluorinated product was well characterized with Raman, IR, SEM, TEM, resistance measurements and x-ray photoelectron spectroscopy (Physical Electronics PHI 5700 XPS using soft monochromatic Al K α (1486.7 eV) x-rays).

3.3 Solvation in Alcohols

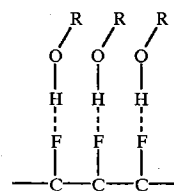
Attempts to solubilize fluorotubes with the "like dissolves like" approach of sonicating and heating them in perfluorinated solvents met with little success. Attempts were also made to solvate them in hydrogen bonding solvents. Recent studies on the hydrogen bonding capabilities of alkyl fluorides suggest that the fluorine in such species are poor hydrogen bond acceptors (Dunitz, et al., R, Eur. J. Chem., 1997, 3(1):89-98; Howard, et al., Tetrahedron, 1996, 52(38): 12613-12622). The F ion, however, is one of the best hydrogen bond acceptors available. The strength of the hydrogen bond formed between HF and F approximates that of a covalent bond (Harrell, et al., JA CS 1964, 86:4497). An

XPS analysis of our fluorinated SWNT product reveals an F 1s peak at a binding energy of 687 eV. Polytetrafluoroethylene has an F binding energy of 691.5 eV. This suggests that the fluorine bonded to the fluorotubes is considerably more ionic than the fluorine present in alkyl fluorides (see Watanabe, et al., Graphite Fluorides, Elsevier: Amsterdam, 1988; p.246). Thus, the increased ionic nature of the C-F bond in the fluorotubes may make the fluorine on it better hydrogen bond acceptors.

Sonication of the fluorinated SWNT material in alcohols was carried out by placing approximately 1 milligram of material into a vial containing approximately 10 mL of alcohol solvent and sonicating for approximately 10 minutes. Sonication was performed by partially immersing the capped vial in a Cole-Parmer ultrasonic cleaner (containing water) operating at 55 kHz. The solvated fluorotubes were then dispersed on a clean mica surface by means of a 3000 rpm rotary spinner (Headway Research, Inc.) and examined with atomic force microscopy (Digital Instruments Multi-mode SPM). The solvated fluorotubes were also analyzed with a Shimadzu model 1601PC UV-vis spectrometer using quartz cuvettes.

Fluorotubes were solvated by sonicating in alcohol solvents including: methanol, ethanol, 2,2,2-trifluoroethanol, 2-propanol, 2-butanol, n-pentanol, n-hexanol, cyclohexanol and n-heptanol. Sonicating the fluorotubes in alcohol solvents produced metastable solutions. These solutions were stable for a couple of days to over one week, depending on the concentration and solvent used. While typical sonication times were around 10 minutes, the heavier solvents (pentanol and up) required slightly longer sonication times in order to fully suspend the tubes. Of the solvents used, 2-propanol and 2-butanol seemed to solvate the fluorotubes the best with the solutions being stable for more than a week. The solubility limit of the solvated "fluorotubes" in 2-propanol is at least 0.1 mg/mL. This solution was stable for slightly less than a week with some particulate matter precipitating out after a few days. This suggests that pushing the solubility limit somewhat decreases the solution's stability or that a super saturated solution can exist for a shorter period of time. All of the other solutions were stable for at least a couple of days before the onset of precipitation. A likely scenario for such solvation would be hydrogen bonding between the alcohol's hydroxyl hydrogen and the nanotubebound fluorine (scheme 1). No evidence of alkoxy substitution (or evolution of HF) was observed.

Scheme 1



Efforts were also made to solvate the fluorotubes in other strong hydrogen bonding solvents like water, diethyl amine, acetic acid and chloroform. While water will not "wet" the fluorotube by itself, it will with the addition of a small amount of acetone. Still, even long sonication times in this water/acetone mixture failed to solvate the fluorotubes. Likewise, neither diethylamine nor acetic acid would solvate the fluorotubes. Chloroform solvated the tubes, but the solution was far less stable than those in alcohol solvents, with the fluorotubes falling out of solution in less than an hour.

The solvated fluorotubes were filtered over a 0.2 micron PTFE filter. Once dry, the fluorotubes could be peeled off the paper to form a freestanding film. This film was then examined by Raman spectroscopy (Jobin Yvon-Spex model HR 460 monochromator coupled with an ISA Spectrum ONE series CCD detector and using 514.5 nm excitation from a Liconix Ar laser) and by EMPA to determine whether or not any reaction had taken place on the basis of the composition of the product. Fluorotubes from all of the solutions (except those in cyclohexanol, n-hexanol and n-heptanol) were examined with atomic force microscopy. FIG. 10 shows an AFM scan of fluorotubes that had been dissolved in 2-butanol and then dispersed on a clean mica surface. This result is fairly typical of all the fluorotube/alcohol solutions that were examined with AFM. Almost all the tubes are believed to be solvated, as few "ropes" (bundles of tubes) are present.

Some of these solutions were examined with ^{19}F -NMR, but this proved to be rather uninformative. It yielded a broad peak centered at around -175 ppm. While this is indicative of fluorine being present, the broadening is due to either a wide variety of F environments (as seen in the inhomogeneous fluorination of C_{60} , Kniaz, et al., *J. Am. Chem. Soc.*, 1993, 115:6060-6064) or of insufficient "tumbling" while in solution. No information regarding the possible hydrogen bonding environments could be obtained with this method.

Filtering a solution of fluorotubes in isopropyl alcohol over a PTFE filter and examining the tubes with EMPA revealed no presence of oxygen and only slightly lower fluorine levels (C/F atomic percent ratio=72/28 compared with 70/30 for the starting material). This would suggest that the solvation process is not the result of a chemical reaction, but is instead the result of hydrogen bonding between the alcohol and the fluorines on the nanotube surface. Analysis of fluorotubes sonicated for much longer times (2 hours) showed reduced levels of fluorine (C/F atomic percent ratio=76/24), yet they remained solvated. Apparently, ultra-sonication can lead to removal of some of the fluorine if allowed to progress long enough. The fluorotubes were sonicated continuously in isopropanol and monitored with UV-vis absorption spectroscopy for sonication time $t=10$ minutes and every 30 minutes after that. After sonication for 40 minutes the solution exhibited an absorption band at 204 nm. This band continued to grow and to red shift to lower energy as the sonication proceeded and fluorine was presumably being eliminated. After sonicating for 130 minutes the peak had increased in intensity and shifted to 237 nm (FIG. 11).

3.4 Reactions in Solution

The present inventors shown that hydrazine acts as a effective defluorinating agent. Anhydrous hydrazine (Aldrich, 98%) was added to the solvated fluorotubes. The reaction mixture was continually stirred with a glass stir bar for a period of about an hour. The reaction mixture was filtered, rinsed with methanol and allowed to dry. This product was then examined with EMPA and Raman spectroscopy. It was also suspended in dimethyl formamide, dispersed on a mica surface and examined with AFM. The instruments and procedures were as above.

Adding anhydrous hydrazine to a solution of fluorotubes in isopropanol caused them to immediately precipitate out of solution. Filtering the solution after letting it sit for an hour yielded a product of very low fluorine content, as determined by EMPA (C/F atomic percent ratio=93/7). Unreacted SWNTs are known to suspend fairly well in DMF. Suspending this product in DMF and dispersing it on a mica surface followed by AFM analysis yielded tubes very reminiscent of the starting material (FIGS. 12, a & b).

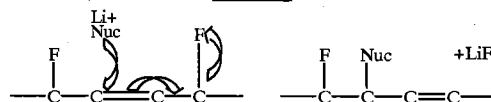
Raman spectroscopy of SWNTs has been well established (Richter, E., et al., *Phys. Rev. Lett.*, 1997, 79(14): 2738-2741; Rao, et al., *Science*, 1997, 275:187-191; Fang, et al., *J. Mat. Res.*, 1998, 13:2405-2411), and it was used as a probe to follow the starting material through the fluorination, sonication and defluorination. Raman spectroscopy on the hydrazine-defluorinated product yields a spectrum similar to the starting material and very different from the fluorinated SWNTs (FIGS. 13; ab & c).

Fluorotubes were also sonicated in a 0.5 M sodium methoxide in methanol solution (Aldrich, A. C. S. reagent) for approximately 10 minutes. The tubes broke up and appeared to be suspended but quickly fell out of solution upon standing. This too was filtered, rinsed and examined with EMPA and EI mass spectroscopy (Finnigan MAT 95).

Sonication of the fluorotubes in a sodium methoxide in methanol solution for two hours resulted in the tubes precipitating out of solution. After the filtered product was rinsed with water (to remove NaF) and methanol, then dried in an oven at 140° C. for half an hour, it was analyzed with EMPA which revealed the C/F/O relative atomic percents to be 79/17/4. This varies considerably from the starting material which had C/F/O relative atomic percents of 66/33.7/0.3 and suggests a product stoichiometry of $\text{C}_{4.4}\text{F}(\text{OCH}_3)_{0.25}$. Pyrolysis of this product with a high temperature probe inside a mass spectrometer, followed by electron ionization, yielded significant quantities of methoxy ions ($m/z=31$) coming off primarily at 650-700° C. as determined by the residual ion current trace. The high temperature for evolution indicates that the methoxy groups seen were originally strongly bonded to the nanotube. If the oxygen ratios seen by EMPA are reflective of the number of methoxy groups present on the nanotube, it may be concluded that the majority of these would have to be bonded to the nanotube side wall, based on the fact that the number of nanotube end carbons is extremely small relative to the number of side wall carbons.

Nucleophilic attack on the fluorinated nanotube by a methoxy anion is a plausible scenario as nucleophilic attack of this type has been well documented in the case of fluorinated fullerenes (Mickelson, et al., *J. Fluorine Chem* 1998, 92(1):59-62; Taylor, et al., *J. Chem. Soc., Chem. Commun.* 1992,665-667). The C-F bonds on fluorinated fullerenes (and carbon nanotubes) are weakened relative to the C-F bonds in alkyl fluorides due to an "eclipsing strain effect" (Taylor, R., *Russian Chemical Bulletin, Engl. Ed.* 1998, 47(5):823-832). A nucleophilic attack of this type is likely to occur via attack on an electropositive carbon beta to a carbon with fluorine attached to it as shown in scheme 2. This is rationalized by the fact that an $\text{S}_{\text{N}}1$ type substitution is energetically unfavorable and backside attack, as in an $\text{S}_{\text{N}}2$ type mechanism, is impossible (Taylor, R *The Chemistry of the Fullerenes* (Edited by R. Taylor), World Scientific Publishing, London, 1995; pp.208-209).

Scheme 2



Molecular Arrays of Single-Wall Carbon Nanotubes

An application of particular interest for a homogeneous population of SWNT molecules is production of a substantially two-dimensional array made up of single-walled nanotubes aggregating (e.g., by van der Waals forces) in substantially parallel orientation to form a monolayer extending

in directions substantially perpendicular to the orientation of the individual nanotubes. Formation of such arrays is substantially enabled by derivatization of both the ends and side walls of nanotubes as is indicated below. Such monolayer arrays can be formed by conventional techniques employing "self-assembled monolayers" (SAM) or Langmuir-Blodgett films, see Hirsch, pp. 75-76. Such a molecular array is illustrated schematically in FIG. 14. In this figure, derivatized nanotubes 1 are bound via interaction of the linking or complexing moiety attached to the nanotube to a substrate 2 having a reactive coating 3 (e.g., gold). Sidewall derivatization in this application can facilitate assembly of the array by enabling the tubes to move effectively together as the array assembles.

Typically, SAMs are created on a substrate which can be a metal (such as gold, mercury or ITO (indium-tin-oxide)). The molecules of interest, here the SWNT molecules, are linked (usually covalently) to the substrate through a linker moiety such as $-S-$, $-S-(CH_2)_n-NH-$, $-SiO_3(CH_2)_3NH-$ or the like. The linker moiety may be bound first to the substrate layer or first to the SWNT molecule (at an open or closed end) to provide for reactive self-assembly. Langmuir-Blodgett films are formed at the interface between two phases, e.g., a hydrocarbon (e.g., benzene or toluene) and water. Orientation in the film is achieved by employing molecules or linkers that have hydrophilic and lipophilic moieties at opposite ends. The configuration of the SWNT molecular array may be homogenous or heterogeneous depending on the use to which it will be put. Using SWNT molecules of the same type and structure provides a homogeneous array of the type shown in FIG. 14. By using different SWNT molecules, either a random or ordered heterogeneous structure can be produced. An example of an ordered heterogeneous array is shown in FIG. 15 where tubes 4 are (n,n), i.e., metallic in structure and tubes 5 are (m,n), i.e., insulating. This configuration can be achieved by employing successive reactions after removal of previously masked areas of the reactive substrate.

Arrays containing from 10^3 up to 10^{10} and more SWNT molecules in substantially parallel relationships can be used per se as a nanoporous conductive molecular membrane, e.g., for use in fuel cells and in batteries such as the lithium ion battery. This membrane can also be used (with or without attachment of a photoactive molecule such as cis-(bisthiacyanato bis (4,4'-dicarboxy-2-2'-bipyridine Ru (II)) to produce a highly efficient photo cell of the type shown in U.S. Pat. No. 5,084,365.

One preferred use of the SWNT molecular arrays of the present invention is to provide a "seed" or template for growth of macroscopic carbon fiber of single-wall carbon nanotubes as described below. The use of a macroscopic cross section in this template is particularly useful for keeping the live (open) end of the nanotubes exposed to feedstock during growth of the fiber. The template array of this invention can be used as formed on the original substrate, cleaved from its original substrate and used with no substrate (the van der Waals forces will hold it together) or transferred to a second substrate more suitable for the conditions of fiber growth.

Where the SWNT molecular array is to be used as a seed or template for growing macroscopic carbon fiber as described below, the array need not be formed as a substantially two-dimensional array. The "seed" array can, for instance, be the end of a fiber of parallel nanotubes in van der Waals contact that has been cut, or a short segment of such a fiber that has been cut from the fiber. For such substrates the surface comprising the ends of must be

prepared to be clean and flat by polishing and or electrochemical etching to achieve a clean, highly planar surface of exposed nanotube ends. Any form of array that presents at its upper surface a two-dimensional array can be employed. In the preferred embodiment, the template molecular array is a manipulatable length of macroscopic carbon fiber as produced below.

Large arrays (i.e., $>10^6$ tubes) also can be assembled using nanopores by combining smaller arrays or by folding linear collections of tubes and/or ropes over (i.e., one folding of a collection of n tubes results in a bundle with 2n tubes). Growth of Nanotubes from "Seeds"

The present invention provides methods for growing continuous carbon fiber from SWNT molecular arrays to any desired length. The carbon fiber which comprises an aggregation of substantially parallel carbon nanotubes may be produced according to this invention by growth (elongation) of a suitable seed molecular array. As used herein, the term "macroscopic carbon fiber" refers to fibers having a diameter large enough to be physically manipulated, typically greater than about 1 micron and preferably greater than about 10 microns.

It is well known that SWNT formation occurs at temperatures between 500 and 2000° C. in which a catalytic particle comprising group VI B or VIII B transition metals (individually or as a mixture) resides at the end of a "growing" SWNT. The catalytic particle interacts with a carbon-bearing feedstock to promote chemical processes by which carbon in the feedstock is converted into carbon organized in the structure known as a SWNT. Once a SWNT of a specific geometry (chirality and diameter) begins to grow, the tube geometry remains fixed. The catalytic tube-growth process is most effectively promoted by catalyst particles of an appropriate size range and chemical composition. Examples in the art indicate that the most effective catalyst particles have diameters approximately equal to those of the growing nanotubes, and that they comprise a single metal or a mixture of metals. An objective of this invention is to provide processes by which a suitable catalyst particle may be formed at the end of an existing SWNT, enabling growth of that tube to be initiated upon introduction of the tube/catalyst-particle assembly to an appropriate environment.

To achieve the objective, the invention provides methods for assembling catalyst particles on the ends of individual fullerene single-wall nanotubes (SWNT) in a way that supports further growth of the SWNT. Deliberate initiation of SWNT growth from such "seed" tubes is useful in that:

- 1) it can act to produce nanotubes that have the same geometry as the "seed" tubes. [It is well known that fullerene single wall nanotubes (SWNT) may be formed with different geometries (different diameters and arrangements of carbon atoms with respect to the tube axis), and that the physical properties (e.g., electrical conductivity) of these tubes generally depend on these geometries]. Control of the tube geometry permits growth of SWNT for applications that require specific material properties.
- 2) It can serve as an enabling process in bulk production of nanotubes;
- 3) It can enable growth of ordered structures of SWNT that have been assembled by other means (e.g., suitable arrays can be formed by conventional techniques employing "self-assembled monolayers" (SAM) or Langmuir-Blodgett films, see Hirsch, pp. 75-76.
- 4) It can be used to grow structural shapes of SWNT material comprising parallel nanotubes all in van der

Waals contact. These materials can have the forms of sheets, I-beams, channels, etc. by appropriately configuring the seed in the shape of the cross section of the desired structural object.

To achieve the objectives and provide the benefits of growth from "seeds," the present invention provides:

- 1) A measured amount of a transition-metal-containing species is chemically attached (by covalent bonding, chemisorption, physisorption or combination thereof) to the sidewall of an individual SWNT segment or to the sidewalls of a group of SWNT segments. A preferred embodiment is one in which the metal is contained as a compound that is stable to exposure to moisture and air. The amount of metal attached to the SWNT segment is determined by the degree of derivatization, which is defined herein as the number of derivative sites per nanometer of tube length. In this invention, the preferred degree of derivatization is approximately 1 per nanometer, and the preferred method of derivatization is covalent bonding of a species that contains a metal atom. Alternatively, the transition metal may be deposited directly on the surface from metal vapor introduced onto the open tube ends of the "seed".
- 2) Chemical or physical processing of the metal or metal-containing species in a way that allows metal atoms to aggregate at or near the end of the tube segment so that the aggregate is a suitable catalyst for enabling growth of the tube when the tube/catalyst assembly is introduced to an appropriate environment.
- 3) Growth of nanotubes of specific geometries (chirality and diameter) by choosing the diameter and chirality of the "seed" tube.
- 4) Growth of organized structures of SWNT (e.g., arrays of tubes with specific relative spacing and orientation of individual tubes, membranes of tubes comprising many parallel tubes closely packed together, and rods or fibers of tubes with parallel axes) in which an initial structure has been assembled by other means, which include the operation of molecule agencies attached to the sidewalls of the SWNTs forming the structure, and the novel compositions of matter so produced.
- 5) Growth of organized structures of SWNT (as 4 above) in which the SWNT all have the same geometry (chirality and diameter) and the composition of matter so produced.
- 6) Growth of organized structures of SWNT (as 4 above) in which the SWNT all have a range of geometries chosen to perform a specific function (e.g., a core of tubes of conducting geometry surrounded by tubes of large-gap semiconducting geometry to effect a small "insulated wire") and the structures so produced.
- 7) Production of "monoclonal" batches of tubes that all have precisely the same geometry because they all are grown from segments of a single tube which has been cut by known techniques and the compositions of matter so produced.

The present invention is further exemplified by the following:

- a) A process in which one cuts segments of SWNT of 0.1 to 1 micron length by, for instance, sonicating the SWNT material in dimethylformamide, selects tube segments of a specific range of length and covalently bonds a chelating agent such as ethylene to the tube wall. These binding sites are sufficiently spaced from one another that the number of chelating agent mol-

ecules is roughly equivalent to the number of metal atoms needed to form an active catalyst cluster at the end of the tube segment. Covalent bonding of various species is described herein, via replacement reactions upon a small fraction of the derivatized sites on fluorinated tubes. A chelating agent is reacted with a fluorinated SWNT so that the chelating agent replaces fluorine on the nanotube, followed by washing the derivatized nanotube with a weak solution of metal ions in water (e.g., Fe^{3+}). The interaction of the Fe and water with the chelating agent will form a complex on the tube surface that is stable under exposure to air and water. The tube material can be heated in a reducing atmosphere (such as H_2). This heating will cause the chelating agent to react by converting to gaseous products, leaving Fe adsorbed on the tube wall, and at appropriate temperatures the Fe will migrate along the tube walls. The tube end presents an irregularity of the surface upon which the Fe is migrating, and the Fe will preferentially collect there as an aggregate suitable for functioning as a catalyst particle for tube growth.

- b) Approaches similar to a) above, but including more complex, multidentate ligands such as ethyldiamine tetra-acetic acid (EDTA) or bipyridine tethered to the side of the SWNT by a covalent linkage or simpler species such as a carboxylate or OH group.
- c) Another means for assembly of a catalytic particle at the end of an SWNT segment involves reaction processes in which chelating agents, other ligands, or metal containing species themselves, are chemically attached to the tube ends (both open and closed). As described above, the tube ends are more active sites and support a broader range of chemical processes than the tube sidewalls. Both ion-exchange and covalent attachment of metal-bearing proteins (e.g. metallothionein) or metal-bearing complexes are possible examples. One can, for example, exchange the metal atoms for the carboxylic acid groups known to exist at the ends of tubes, directly attached metal bearing proteins or other metal-containing species with the tube ends. If necessary further processes can enable deposition of additional metal at the ends of the tube segments. The amount of metal is simply determined by the usual methods of control of the reagent concentrations, temperatures, and reaction times. Here, again, aggregates of metal atoms of the appropriate size are formed at the end of selected SWNT segments, and can serve as catalysts for tube growth under the appropriate conditions.
- d) Formation of arrays of SWNT wherein the array formation is enabled and controlled by species attached to the tube sidewalls. This species that enables array formation may be attached to the tube by covalent bonding, chemisorption, adsorption, or a combination thereof. This aspect of this invention:
 - i) enables and controls organization of SWNT segments into organized structures and
 - ii) admits metal-containing species or metal atoms or ions to the tube sidewalls in a way that under appropriate chemical processing the metal particles may migrate to the tube ends and form catalysts for further SWNT growth.

The first step in the growth process is to open the growth end of the SWNTs in the molecular array. This can be accomplished as described above with an oxidative and/or electrochemical treatment. Next, a transition metal catalyst

is added to the open-ended seed array. The transition metal catalyst can be any transition metal that will cause conversion of the carbon-containing feedstock described below into highly mobile carbon radicals that can rearrange at the growing edge to the favored hexagon structure. Suitable materials include transition metals, and particularly the Group VI B or VIII B transition metals, i.e., chromium (Cr), molybdenum (Mo), tungsten (W), iron (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt). Metals from the lanthanide and actinide series may also be used. Preferred are Fe, Ni, Co and mixtures thereof. Most preferred is a 50/50 mixture (by weight) of Ni and Co.

The catalyst should be present on the open SWNT ends as a metal cluster containing from about 10 metal atoms up to about 200 metal atoms (depending on the SWNT molecule diameter). Typically, the reaction proceeds most efficiently if the catalyst metal cluster sits on top of the open tube and does not bridge over adjacent tubes. Preferred are metal clusters having a cross-section equal to from about 0.5 to about 1.0 times the tube diameter (e.g., about 0.7 to 1.5 nm).

In the preferred process, the catalyst is formed, in situ, on the open tube ends of the molecular array by a vacuum deposition process. Any suitable equipment, such as that used in Molecular Beam Epitaxy (MBE) deposition, can be employed. One such device is a Küdsen Effusion Source Evaporator. It is also possible to effect sufficient deposition of metal by simply heating a wire in the vicinity of the tube ends (e.g., a Ni/CO wire or separate Ni and CO wires) to a temperature below the melting point at which enough atoms evaporate from one wire surface (e.g., from about 900 to about 1300° C.). The deposition is preferably carried out in a vacuum with prior outgassing. Vacuums of about 10^{-6} to 10^{-8} Torr are suitable. The evaporation temperature should be high enough to evaporate the metal catalyst. Typically, temperatures in the range of 1500 to 2000° C. are suitable for the Ni/Co catalyst of the preferred embodiment. In the evaporation process, the metal is typically deposited as monolayers of metal atoms. From about 1–10 monolayers will generally give the required amount of catalyst. The deposition of transition metal clusters on the open tube tops can also be accomplished by laser vaporization of metal targets in a catalyst deposition zone.

The actual catalyst metal cluster formation at the open tube ends is carried out by heating the tube ends to a temperature high enough to provide sufficient species mobility to permit the metal atoms to find the open ends and assemble into clusters, but not so high as to effect closure of the tube ends. Typically, temperatures of up to about 500° C. are suitable. Temperatures in the range of about 400–500° C. are preferred for the Ni/Co catalysts system of one preferred embodiment.

In a preferred embodiment, the catalyst metal cluster is deposited on the open nanotube end by a docking process that insures optimum location for the subsequent growth reaction. In this process, the metal atoms are supplied as described above, but the conditions are modified to provide reductive conditions, e.g., at 800° C., 10 millitorr of H_2 for 1 to 10 minutes. These conditions cause the metal atom clusters to migrate through the system in search of a reactive site. During the reductive heating the catalyst material will ultimately find and settle on the open tube ends and begin to etch back the tube. The reduction period should be long enough for the catalyst particles to find and begin to etch back the nanotubes, but not so long as to substantially etch away the tubes. By changing to the above-described growth conditions, the etch-back process is reversed. At this point,

the catalyst particles are optimally located with respect to the tube ends since they already were catalytically active at those sites (albeit in the reverse process).

The catalyst can also be supplied in the form of catalyst precursors which convert to active form under growth conditions such as oxides, other salts or ligand stabilized metal complexes. As an example, transition metal complexes with alkylamines (primary, secondary or tertiary) can be employed. Similar alkylamine complexes of transition metal oxides also can be employed. The catalyst can also be added to the free ends by causing migration of metal atoms derived from side wall pendant groups added as described above.

In the next step of the process of the present invention, the SWNT molecular array with catalyst deposited on the open tube ends is subjected to tube growth (extension) conditions. This may be in the same apparatus in which the catalyst is deposited or a different apparatus. The apparatus for carrying out this process will require, at a minimum, a source of carbon-containing feedstock and a means for maintaining the growing end of the continuous fiber at a growth and annealing temperature where carbon from the vapor can be added to the growing ends of the individual nanotubes under the direction of the transition metal catalyst. Typically, the apparatus will also have means for continuously collecting the carbon fiber. The process will be described for illustration purposes with reference to the apparatus shown in FIGS. 16 and 17.

The carbon supply necessary to grow the SWNT molecular array into a continuous fiber is supplied to the reactor 10, in gaseous form through inlet 11. The gas stream should be directed towards the front surface of the growing array 12. The gaseous carbon-containing feedstock can be any hydrocarbon or mixture of hydrocarbons including alkyls, acyls, aryls, aralkyls and the like, as defined above. Preferred are hydrocarbons having from about 1 to 7 carbon atoms. Particularly preferred are methane, ethane, ethylene, acetylene, acetone, propane, propylene and the like. Most preferred is ethylene. Carbon monoxide may also be used and in some reactions is preferred. Use of CO feedstock with transition metal catalysts is believed to follow a different reaction mechanism than that proposed for most other feedstock gasses. See Dai, et al., 1996.

The feedstock concentration is preferably as chosen to maximize the rate of reaction, with higher concentrations of hydrocarbon giving faster growth rates. In general, the partial pressure of the feedstock material (e.g., ethylene) can be in the 0.001 to 1000.0 Torr range, with values in the range of about 1.0 to 10 Torr being preferred. The growth rate is also a function of the temperature of the growing array tip as described below, and as a result growth temperatures and feed stock concentration can be balanced to provide the desired growth rates. A preferred feedstock in many instances is CO, in which case the optimal pressures are in the range of 10 to 100 atmospheres.

It is not necessary or preferred to preheat the carbon feedstock gas, since unwanted pyrolysis at the reactor walls can be minimized thereby. The only heat supplied for the growth reaction should be focused at the growing tip of the fiber 12. The rest of the fiber and the reaction apparatus can be kept at room temperature. Heat can be supplied in a localized fashion by any suitable means. For small fibers (<1 mm in diameter), a laser 13 focused at the growing end is preferred (e.g., a C—W laser such as an argon ion laser beam at 514 nm). For larger fibers, heat can be supplied by microwave energy or R—F energy, again localized at the growing fiber tip. Any other form of concentrated electro-

magnetic energy that can be focused on the growing tip can be employed (e.g., solar energy). Care should be taken, however, to avoid electromagnetic radiation that will be absorbed to any appreciable extent by the feedstock gas.

The SWNT molecular array tip should be heated to a temperature sufficient to cause growth and efficient annealing of defects in the growing fiber, thus forming a growth and annealing zone at the tip. In general, the upper limit of this temperature is governed by the need to avoid pyrolysis of the feedstock and fouling of the reactor or evaporation of the deposited metal catalyst. For most feedstocks and catalysts, this is below about 1300° C. The lower end of the acceptable temperature range is typically about 500° C., depending on the feedstock and catalyst efficiency. Preferred are temperatures in the range of about 500° C. to about 1200° C. More preferred are temperatures in the range of from about 700° C. to about 1200° C. Temperatures in the range of about 900° C. to about 1100° C. are the most preferred, since at these temperatures the best annealing of defects occurs. The temperature at the growing end of the cable is preferably monitored by, and controlled in response to, an optical pyrometer 14, which measures the incandescence produced. While not preferred due to potential fouling problems, it is possible under some circumstances to employ an inert sweep gas such as argon or helium.

In general, pressure in the growth chamber can be in the range of 1 millitorr to about 1 atmosphere. The total pressure should be kept at 1 to 2 times the partial pressure of the carbon feedstock. A vacuum pump 15 may be provided as shown. It may be desirable to recycle the feedstock mixture to the growth chamber. As the fiber grows it can be withdrawn from the growth chamber 16 by a suitable transport mechanism such as drive roll 17 and idler roll 18. The growth chamber 16 is in direct communication with a vacuum feed lock zone 19.

The pressure in the growth chamber can be brought to atmospheric, if necessary, in the vacuum feed lock by using a series of chambers 20. Each of these chambers is separated by a loose TEFLON O-ring seal 21 surrounding the moving fiber. Pumps 22 effect the differential pressure equalization. A take-up roll 23 continuously collects the room temperature carbon fiber cable. Product output of this process can be in the range of 10^{-3} to 10^1 feet per minute or more. By this process, it is possible to produce tons per day of continuous carbon fiber made up of SWNT molecules.

Growth of the fiber can be terminated at any stage (either to facilitate manufacture of a fiber of a particular length or when too many defects occur). To restart growth, the end may be cleaned (i.e., reopened) by oxidative etching (chemically or electrochemically). The catalyst particles can then be reformed on the open tube ends, and growth continued.

The molecular array (template) may be removed from the fiber before or after growth by macroscopic physical separation means, for example by cutting the fiber with scissors to the desired length. Any section from the fiber may be used as the template to initiate production of similar fibers.

The continuous carbon fiber of the present invention can also be grown from more than one separately prepared molecular array or template. The multiple arrays can be the same or different with respect to the SWNT type or geometric arrangement in the array. Large cable-like structures with enhanced tensile properties can be grown from a number of smaller separate arrays as shown in FIG. 18. In addition to the masking and coating techniques described above, it is possible to prepare a composite structure, for example, by surrounding a central core array of metallic

SWNTs with a series of smaller circular non-metallic SWNT arrays arranged in a ring around the core array as shown in FIG. 19.

Not all the structures contemplated by this invention need be round or even symmetrical in two-dimensional cross section. It is even possible to align multiple molecular array seed templates in a manner as to induce nonparallel growth of SWNTs in some portions of the composite fiber, thus producing a twisted, helical rope, for example. It is also possible to catalytically grow macroscopic carbon fiber in the presence of an electric field to aid in alignment of the SWNTs in the fibers, as described above in connection with the formation of template arrays.

Random Growth of Carbon Fibers from SWNTs

While the continuous growth of ordered bundles of SWNTs described above is desirable for many applications, it is also possible to produce useful compositions comprising a randomly oriented mass of SWNTs, which can include individual tubes, ropes and/or cables. The random growth process has the ability to produce large quantities, i.e., tons per day, of SWNT material.

In general the random growth method comprises providing a plurality of SWNT seed molecules that are supplied with a suitable transition metal catalyst as described above, including the use of side wall derivatization to supply the catalyst moiety and subjecting the seed molecules to SWNT growth conditions that result in elongation of the seed molecule by several orders of magnitude, e.g., 10^2 to 10^{10} or more times its original length.

The seed SWNT molecules can be produced as described above, preferably in relatively short lengths, e.g., by cutting a continuous fiber or purified bucky paper. In a preferred embodiment, the seed molecules can be obtained after one initial run from the SWNT felt produced by this random growth process (e.g., by cutting). The lengths do not need to be uniform and generally can range from about 5 nm to 10 μ m in length.

These SWNT seed molecules may be formed on macroscale or nanoscale supports that do not participate in the growth reaction. In another embodiment, SWNTs or SWNT structures can be employed as the support material/seed. For example, the self assembling techniques described below can be used to form a three-dimensional SWNT nanostructure. Nanoscale powders produced by these techniques have the advantage that the support material can participate in the random growth process.

The supported or unsupported SWNT seed materials can be combined with a suitable growth catalyst as described above, by opening SWNT molecule ends and depositing a metal atom cluster. Alternatively, the growth catalyst can be provided to the open end or ends of the seed molecules by evaporating a suspension of the seeds in a suitable liquid containing a soluble or suspended catalyst precursor. For example, when the liquid is water, soluble metal salts such as $\text{Fe}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$ or $\text{Co}(\text{NO}_3)_2$ and the like may be employed as catalyst precursors. In order to insure that the catalyst material is properly positioned on the open end(s) of the SWNT seed molecules, it may be necessary in some circumstances to derivatize the SWNT ends with a moiety that binds the catalyst nanoparticle or more preferably a ligand-stabilized catalyst nanoparticle.

In the first step of the random growth process the suspension of seed particles containing attached catalysts or associated with dissolved catalyst precursors is injected into an evaporation zone where the mixture contacts a sweep gas flow and is heated to a temperature in the range of 250–500° C. to flash evaporate the liquid and provide an entrained

reactive nanoparticle (i.e., seed/catalyst). Optionally this entrained particle stream is subjected to a reduction step to further activate the catalyst (e.g., heating from 300–500° C. in H₂). A carbonaceous feedstock gas, of the type employed in the continuous growth method described above, is then introduced into the sweep gas/active nanoparticle stream and the mixture is carried by the sweep gas into and through a growth zone.

The reaction conditions for the growth zone are as described above, i.e., 500–1000° C. and a total pressure of about one atmosphere. The partial pressure of the feedstock gas (e.g., ethylene, CO) can be in the range of about 1 to 100 Torr for ethylene or 1 to 100 atmospheres for CO. The reaction with pure carbon or hydrocarbon feedstocks is preferably carried out in a tubular reactor through which a sweep gas (argon) flows.

The growth zone may be maintained at the appropriate growth temperature by 1) preheating the feedstock gas, 2) preheating the sweep gas, 3) externally heating the growth zone, 4) applying localized heating in the growth zone, e.g., by laser or induction coil, or any combination of the foregoing.

Downstream recovery of the product produced by this process can be effected by known means such as filtration, centrifugation and the like. Purification may be accomplished as described above. Felts made by this random growth process can be used to make composites, e.g., with polymers, epoxies, metals, carbon (i.e., carbon/carbon materials) and high -T_c superconductors for flux pinning.

What is claimed is:

1. A method comprising the steps of:

- i. reacting single wall carbon nanotubes with a fluorinating agent; and
- ii. dispersing the single wall carbon nanotubes in a solvent.

2. The method of claim 1 further comprising the step of reacting the single wall carbon nanotubes with substituents to covalently bond the substituents to the carbon nanotubes.

3. The method of claim 2, wherein the substituents are selected from the group consisting of alkyl, acyl, aryl, aralkyl, halogen, substituted thiol, unsubstituted thiol, substituted amino, unsubstituted amino, hydroxy, and OR', wherein R' is selected from the group consisting of hydrogen, alkyl, acyl, aryl, aralkyl, halogen, substituted thiol, unsubstituted thiol, substituted amino, unsubstituted amino, a linear carbon chain, and a cyclic carbon chain.

4. The method of claim 3, wherein the linear carbon chain or the cyclic carbon chain or both is substituted with at least one heteroatom.

5. The method of claim 3, wherein the linear carbon chain or the cyclic carbon chain or both is substituted with one or more of the group consisting of =O, =S, hydroxy, an aminoalkyl, an amino acid, and a peptide of 2–8 amino acids.

6. The method of claim 1, wherein the fluorinating agent is selected from the group consisting of fluorine, ClF₃, BrF₃, IF₅, XeF₂, XeF₄, AgF₂, and MnF₃.

7. The method of claim 1, wherein the dispersing step comprises sonication.

8. The method of claim 1, wherein the solvent is selected from the group consisting of an alcohol, CHCl₃, and dimethylformamide.

9. The method of claim 8, wherein the alcohol is selected from the group consisting of methanol, ethanol, 2,2,2-trifluoroethanol, 2-propanol, 2-butanol, n-pentanol, n-hexanol, cyclohexanol and n-heptanol.

10. The method of claim 1, further comprising the step of defluorinating the reacted carbon nanotubes.

11. The method of claim 1, further comprising the step of defluorinating the reacted carbon nanotubes with hydrazine.

12. The method of claim 2, wherein the substituents are part of an organometallic compound before being covalently bonded to the sidewall of the single wall carbon nanotube.

13. The method of claim 12, wherein said organometallic compound is a compound of an alkali metal, said compound having from 1 to 20 carbon atoms and said compound being selected from the group consisting of a substituted alkyl compound of the alkali metal, an unsubstituted alkyl of the alkali metal, a substituted aryl compound of the alkali metal, and an unsubstituted aryl compound of the alkali metal.

14. The method of claim 13, wherein the alkali metal is sodium or lithium.

15. The method of claim 2, further comprising removing residual fluorine from the single wall carbon nanotube subsequent to bonding the substituent to the single wall carbon nanotube.

16. A method comprising the steps of:

- i. reacting carbon nanotubes with a fluorinating agent;
- ii. reacting the carbon nanotubes with substituents to covalently bond the substituents to the carbon nanotubes; and
- iii. dispersing the carbon nanotubes in a solvent.

17. The method of claim 16, wherein the substituents are selected from the group consisting of alkyl, acyl, aryl, aralkyl, halogen, substituted thiol, unsubstituted thiol, substituted amino, unsubstituted amino, hydroxy, and OR', wherein R' is selected from the group consisting of hydrogen, alkyl, acyl, aryl, aralkyl, halogen, substituted thiol, unsubstituted thiol, substituted amino, unsubstituted amino, a linear carbon chain, and a cyclic carbon chain.

18. The method of claim 17, wherein the linear carbon chain or the cyclic carbon chain or both is substituted with at least one heteroatom.

19. The method of claim 17, wherein the linear carbon chain or the cyclic carbon chain or both is substituted with one or more of the group consisting of =O, =S, hydroxy, an aminoalkyl, an amino acid, and a peptide of 2–8 amino acids.

20. The method of claim 16, wherein the fluorinating agent is selected from the group consisting of fluorine, ClF₃, BrF₃, IF₅, XeF₂, XeF₄, AgF₂, and MnF₃.

21. A method comprising the steps of:

- i. reacting carbon nanotubes with a fluorinating agent; and
- ii. dispersing the carbon nanotubes in a solvent, wherein the dispersing step comprises sonication.

22. A method comprising the steps of:

- i. reacting carbon nanotubes with a fluorinating agent; and
- ii. dispersing the carbon nanotubes in a solvent, wherein the solvent is selected from the group consisting of an alcohol, CHCl₃, and dimethylformamide.

23. The method of claim 22, wherein the alcohol is selected from the group consisting of methanol, ethanol, 2,2,2-trifluoroethanol, 2-propanol, 2-butanol, n-pentanol, n-hexanol, cyclohexanol and n-heptanol.

24. A method comprising the steps of:

- i. reacting carbon nanotubes with a fluorinating agent;
- ii. dispersing the carbon nanotubes in a solvent; and
- iii. defluorinating the reacted carbon nanotubes.

25. A method comprising the steps of:

- i. reacting carbon nanotubes with a fluorinating agent;
- ii. dispersing the carbon nanotubes in a solvent; and
- iii. defluorinating the reacted carbon nanotubes with hydrazine.

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26. The method of claim 16, wherein the substituents are part of an organometallic compound before being covalently bonded to the sidewall of the carbon nanotube.

27. The method of claim 26, wherein said organometallic compound is a compound of an alkali metal, said compound having from 1 to 20 carbon atoms and said compound being selected from the group consisting of a substituted alkyl compound of the alkali metal, an unsubstituted alkyl of the alkali metal, a substituted aryl compound of the alkali metal, and an unsubstituted aryl compound of the alkali metal.

28. The method of claim 27, wherein the alkali metal is sodium or lithium.

29. The method of claim 16, further comprising removing residual fluorine from the reacted carbon nanotube subsequent to bonding the substituent to the carbon nanotube.

30. A method for preparing single wall carbon nanotubes having substituents attached to a sidewall of the single wall carbon nanotubes comprising:

- i. reacting the single wall carbon nanotubes with a fluorinating agent;
- ii. solvating the fluorine derivatized single wall carbon nanotubes;
- iii. reacting the fluorine derivatized single wall carbon nanotubes with substituents; and
- iv. recovering the single wall carbon nanotubes with the substituents covalently bonded to carbon atoms of the sidewall of the nanotubes.

31. The method of claim 30, wherein the substituents are selected from the group consisting of alkyl, acyl, aryl, aralkyl, halogen, substituted thiol, unsubstituted thiol, substituted amino, unsubstituted amino, hydroxy, and OR', wherein R' is selected from the group consisting of hydrogen, alkyl, acyl, aryl, aralkyl, halogen, substituted thiol, unsubstituted thiol, substituted amino, unsubstituted amino, a linear carbon chain, and a cyclic carbon chain.

32. The method of claim 31, wherein the linear carbon chain or the cyclic carbon chain or both is substituted with at least one heteroatom.

33. The method of claim 31, wherein the linear carbon chain or the cyclic carbon chain or both is substituted with one or more of the group consisting of =O, =S, hydroxy, an aminoalkyl, an amino acid, and a peptide of 2-8 amino acids.

34. The method of claim 30, wherein the fluorinating agent is selected from the group consisting of fluorine, ClF_3 , BrF_3 , IF_5 , XeF_2 , XeF_4 , AgF_2 , and MnF_3 .

35. The method of claim 30, wherein the substituents are part of an organometallic compound before being covalently bonded to the sidewall of the single wall carbon nanotube.

36. The method of claim 30, wherein said organometallic compound is a compound of an alkali metal, said compound having from 1 to 20 carbon atoms and said compound being selected from the group consisting of a substituted alkyl compound of the alkali metal, an unsubstituted alkyl of the alkali metal, a substituted aryl compound of the alkali metal, and an unsubstituted aryl compound of the alkali metal.

37. The method of claim 36, wherein the alkali metal is sodium or lithium.

38. The method of claim 30, further comprising removing residual fluorine from the single wall carbon nanotube subsequent to bonding the substituent to the single wall carbon nanotube.

39. The method of claim 30, wherein the amount of substituent bonded to carbon atoms of the single wall carbon nanotubes is at a substituent to carbon ratio of from (a) one substituent to about 26 carbon atoms to (b) one substituent to about two carbon atoms.

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40. The method of claim 39, wherein the amount of substituent bonded to the carbon atoms of the single wall carbon nanotubes is at the substituent to carbon ratio of from (a) one substituent to about ten carbon atoms to (b) one substituent to about two carbon atoms.

41. The method of claim 40, wherein the amount of substituent bonded to the carbon atoms of the single wall carbon nanotubes is at a substituent to carbon ratio of from (a) one substituent to about three carbon atoms to (b) one substituent to about two carbon atoms.

42. A method for preparing carbon nanotubes having substituents attached to the sidewalls of the carbon nanotubes comprising:

- i. reacting the carbon nanotubes with a fluorinating agent;
- ii. solvating the fluorine derivatized carbon nanotubes;
- iii. reacting the fluorine derivatized carbon nanotubes with substituents; and
- iv. recovering the carbon nanotubes with the substituents covalently bonded to carbon atoms of the sidewall of the nanotubes.

43. A method of forming a solution of single wall carbon nanotubes comprising the steps of:

- i. derivatizing single wall carbon nanotubes with a fluorinating agent; and
- ii. dispersing the plurality of single wall carbon nanotubes in a solvent.

44. A method of forming a solution of single wall carbon nanotubes comprising the steps of:

- i. fluorinating the single wall carbon nanotubes with a fluorinating agent at a reaction temperature up to about 500° C., and
- ii. dispersing the single wall carbon nanotubes in a solvent, wherein the solvent is selected from the group consisting of an alcohol, CHCl_3 , and dimethylformamide.

45. A method of forming a solution of single wall carbon nanotubes comprising the steps of:

- i. covalently bonding substituents to the single wall carbon nanotubes, and
- ii. dispersing the single wall carbon nanotubes in a solvent.

46. The method of claim 45, wherein the dispersing step comprises sonication.

47. The method of claim 45, wherein the solvation step comprises using a solvent selected from the group consisting of an alcohol, CHCl_3 , and dimethylformamide.

48. The method of claim 47, wherein the alcohol is selected from the group consisting of methanol, ethanol, 2,2,2-trifluoroethanol, 2-propanol, 2-butanol, n-pentanol, n-hexanol, cyclohexanol and n-heptanol.

49. The method of claim 45, wherein the substituents are selected from the group consisting of alkyl, acyl, aryl, aralkyl, halogen, substituted thiol, unsubstituted thiol, substituted amino, unsubstituted amino, hydroxy, and OR', wherein R' is selected from the group consisting of hydrogen, alkyl, acyl, aryl, aralkyl, halogen, substituted thiol, unsubstituted thiol, substituted amino, unsubstituted amino, a linear carbon chain, and a cyclic carbon chain.

50. The method of claim 49, wherein the linear carbon chain or the cyclic carbon chain or both is substituted with at least one heteroatom.

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51. The method of claim 49, wherein the linear carbon chain or the cyclic carbon chain or both is substituted with one or more of the group consisting of =O, =S, hydroxy, an aminoalkyl, an amino acid, and a peptide of 2-8 amino acids.

52. The method of claim 49, wherein the amount of substituent bonded to carbon atoms of the single wall carbon nanotubes is at a substituent to carbon ratio of from (a) one substituent to about 26 carbon atoms to (b) one substituent to about two carbon atoms.

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53. The method of claim 52, wherein the amount of substituent bonded to the carbon atoms of the single wall carbon nanotubes is at the substituent to carbon ratio of from (a) one substituent to about ten carbon atoms to (b) one substituent to about two carbon atoms.

54. The method of claim 53, wherein the amount of substituent bonded to the carbon atoms of the single wall carbon nanotubes is at the substituent to carbon ratio of from (a) one substituent to about three carbon atoms to (b) one substituent to about two carbon atoms.

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